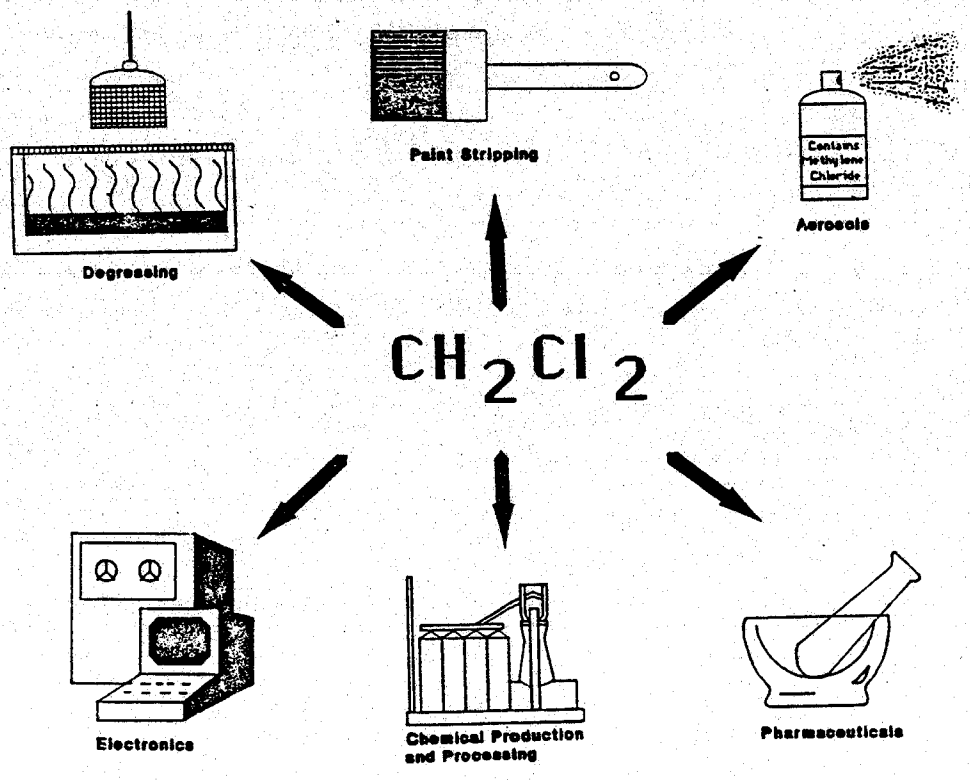
TECHNICAL SUPPORT DOCUMENT

PROPOSED IDENTIFICATION OF METHYLENE CHLORIDE AS A TOXIC AIR CONTAMINANT

Part A Report



State of California
Air Resources Board
Stationary Source Division

May 1989

FINAL DRAFT

TECHNICAL SUPPORT DOCUMENT

REPORT TO THE AIR RESOURCES BOARD ON METHYLENE CHLORIDE

Prepared by the Staff of the Air Resources Board

Principal Investigators:
Richard Corey
John Marconi

Contributing Authors:
Ron Rothacker
Paul Allen
Marci Nystrom

Reviewed and Approved by:

Joan Denton, Manager
Substance Evaluation Section;

Robert Barham, Chief
Toxic Air Contaminant Identification Branch;

Peter D. Venturini, Chief
Stationary Source Division

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May 1989

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FINAL DRAFT

REPORT TO THE AIR RESOURCES BOARD ON METHYLENE CHLORIDE

Part A - Public Exposure to, Atmospheric fate of, and Sources of Atmospheric Methylene Chloride in California

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I.

INTRODUCTION

Methylene chloride is one of the family of chemicals known as chlorinated hydrocarbons and has the chemical formula CH_2Cl_2. It has several chemical synonyms and trade names including: dichloromethane, methylene dichloride, methane dichloride, Aerothene NM, Somethine®, F30®, Freon 30®, and F-30®. It is used in California in the following products and processes: paint removers, aerosols, degreasing operations, pesticide manufacturing and use, photographic film processing, pharmaceuticals, food processing, chemical processing and production, and photoresist stripping. Methylene chloride is also used in a variety of miscellaneous applications primarily for its solvent properties.

This report is an evaluation of methylene chloride uses, emission sources, ambient and indoor concentrations, and population exposure in California. Also included are discussions of the atmospheric fate and the physical properties of methylene chloride. The Air Resources Board will consider the findings of this report together with the health related effects findings of the Department of Health Services to determine if methylene chloride should be identified as a toxic air contaminant (TAC).

The ARB is the state agency responsible for the identification of TACs in their non-pesticidal uses. State law defines a TAC as an air pollutant which the Air Resources Board (ARB) or the Department of Food and Agriculture (DFA) finds "...may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health" (California Health and Safety Code Section 39655).

Because all of the methylene chloride consumed for many use categories is emitted to the atmosphere, annual emissions in California are significant. Once in the atmosphere methylene chloride is persistent with an atmospheric lifetime which may be on the order of several months. The ARB's monitoring network has detected methylene

chloride throughout the state. Monitoring results show that the highest concentrations occur in the South Coast Air Basin where the majority of the state's identified emission sources and roughly 40 percent of the state's population are located.

This report presents estimates of the general population's exposure to methylene chloride. The results show that people living within the studied areas (approximately 80 percent of the state's population) are exposed to airborne methylene chloride throughout the year. Because there is some uncertainty about the absolute concentrations that people are exposed to, a range of concentrations is presented. In addition, exposure was estimated for people living near methylene chloride emission sources in the South Coast Air Basin. Modeling results show that people living near emission sources are exposed to levels of methylene chloride that are higher than average concentrations in that air basin.

Although the data are limited, it appears that indoor exposure to methylene chloride as well as exposure from the use of consumer products may represent the most important source of exposure for some people. However, in order to adequately characterize these exposures will require further research.

II.

EXPOSURE TO METHYLENE CHLORIDE

A. AMBIENT MONITORING IN CALIFORNIA

In January 1985, the Air Resources Board (ARB) initiated ambient monitoring for methylene chloride at 20 monitoring stations located throughout California. ARB's monitoring and Laboratory Division (MLD) carried out the sampling and analysis for the nine monitoring stations located in southern California and for the eleven monitoring stations located in northern California.

For each monitoring station, approximately two samples are taken each month. Samples are collected in 30 liter Tedlar bags over a twenty-four hour period using a low volume sampler. Samples are subsequently preconcentrated and analyzed by gas chromatography employing an electron capture detector. Resultant peaks are identified by retention time and quantified by reference to calibration standards. The ARB's limit of detection (LOD) for the analytical method for methylene chloride has been determined to be 1.0 ppb. The precision for the analytical method has been determined and shows that one standard deviation for the analysis is on the order of ±10 percent. However, the overall error associated with the sampling and analysis method has not been determined. The standard operating procedures for the sampling and analysis conducted by ARB are provided in Appendix I.

Monitoring data for the time period of January 1985 through March 1987 have been evaluated for this report. At each monitoring station there are some months for which no data have been reported. For these months either no samples were collected or laboratory staff have judged that the sampling and analysis did not meet ARB's quality control criteria and therefore the data were deleted. Table II-1 presents the months for which data are available and the total number of samples reported for each station during the twenty-seven month period.

B. CONCENTRATIONS IN CALIFORNIA

Since the monitoring network was instituted in January of 1985, methylene chloride has been detected at each of the 20 monitoring

TABLE II-1

SUMMARY OF AVAILABILITY OF METHYLENE CHLORIDE DATA
DURING JANUARY 1985 THROUGH MARCH 1987*

Air Basin Site Location	1985 JFMAMJJASOND	1986 JFMAMJJASOND	1987 JFM	# of Samples
SOUTHERN CALIFORNIA SITES				
SOUTH COAST AIR BASIN:				
El Monte	●●●●●●○○●●●●	●○●●●●●●●●●●	●●●	68
Los Angeles	●●●●●●○○●●●●	●○●●●●●●●●●●	●●●	55
No. Long Beach	●●●●●○○○●●●●	●○●●●●●●●●●●	●●●	53
Riverside	●●●●●●○○●●●●	●●●●●●●●●●●●	●●●	52
Upland	●●●●●●○○●●●●	●●●●●●●●●●●●	●●●	54
SOUTH CENTRAL COAST AIR BASIN:				
Santa Barbara	●●●●●○○○●●●●	●○●●●●●●●●●●	●●●	46
Simi Valley	●●●●●○○○●●●●	●●●●●●●●●●●●	●●●	56
SAN DIEGO AIR BASIN:				
Chula Vista	●●●●●●○○●●●●	●○●●●●●●●●●●	●●●	56
El Cajon	●●●●●●○○●●●●	●○●●●●●●●●●●	○●●	50
NORTHERN CALIFORNIA SITES				
SAN FRANCISCO BAY AREA AIR BASIN:				
Concord	○○○○○○○●●●●●	●●○○○●●●●●●○	●●●	24
Fremont	○○○○○○○●●●●●	●●○○○●○○●●●○	●●●	26
Richmond	○○○○○○○●●●●●	●●○○○●●●●●●●	●●●	29
San Francisco	○○○○○○○●○●●●	○●○○○●●●●●●●	○●●	19
San Jose	○○○○○○○●●●●●	●●○○○●●○●●●●	●●●	28
SAN JOAQUIN VALLEY AIR BASIN:				
Bakersfield	○○○○○○○●●●●●	●●○○○●●●○●○●	●○●	30
Fresno	○○○○○○○●●●●●	●●○○○●○●●●●●	●●●	32
Merced	○○○○○○○●●●●●	●●○○○○○●●●●●	●●●	26
Modesto	○○○○○○○●●●●●	●●○○○●○●●●●●	●●●	28
Stockton	○○○○○○○●●●●●	●●○○○●●●●●●●	●●●	34
SACRAMENTO VALLEY AIR BASIN:				
Citrus Heights	○○○○○○○●●●●●	●●○○○●○●●●●●	●●●	31

* A solid dot indicates at least one sample is available for that particular month.

stations in California. Summary statistics have been compiled using all the available monitoring data for the twenty-seven month period covering January 1985 through March 1987.

As stated earlier, for each of the monitoring stations there are months for which data are not available. Thus, the number of samples representing each month of the year for each station is variable. For instance, no data are available for the second calendar quarter at the Merced station for 1985, 1986 and 1987. If a seasonal variation of the ambient concentration occurs each year, the variation in the number of samples available for each month could bias the overall mean concentration. However, after evaluating the monthly means in each air basin, ARB staff did not detect any discernable seasonal variation in the ambient concentration of methylene chloride.

For each monitoring station Table II-2 reports the number of samples in the data base, the mean concentration for the samples, the peak 24-hour average concentrations measured, the percentage of samples below the LOD, and an estimate of the concentration of the samples below the LOD.

The number of samples available at each station ranges from 19 to 68 with a total of 797 samples reported for the 20 station network. Forty-eight percent of the 797 samples are below the LOD . However, for individual monitoring stations the percentage of samples below the LOD ranges from 16 percent at the El Monte station to 91 percent at the Stockton station. In general, northern California stations have a higher percentage of samples below the LOD than do southern California stations.

Calculation of mean concentrations for stations is complicated by the presence of concentrations below the LOD. The concentrations below the LOD must be somehow included in the calculation although their exact values are not known.

Staff has used a method proposed by Gleit (1985) to calculate the means. Gleit's method assumes that the sample of concentrations is a random sample from a normal distribution. Data that are judged not to be normally distributed may be transformed to approximate normality. Inspection of the methylene chloride data suggested that they were lognormally distributed, and Gleit's method was applied to the logarithms of these data. The calculated means were then transformed back to the original units.

Gleit's method accounts for the concentrations below the LOD by setting them equal to the "below-LOD mean", the mean of the portion of the normal distribution below the LOD. Setting the unknown concentrations to their average value seems intuitively reasonable, and

TABLE II-2

SUMMARY STATISTICS OF THE JANUARY 1985 THROUGH MARCH 1987
METHYLENE CHLORIDE MONITORING DATA

Air Basin Site Location	Number of Samples	Mean Concentration[a] (ppb)	Peak Concentration (ppb)	Percentage of Samples Below LOD[b]	Estimated Concentration for Samples below the LOD[b] (ppb)
SOUTHERN CALIFORNIA SITES					
SOUTH COAST AIR BASIN:					
El Monte	68	2.5	7.0	16	0.8
Los Angeles	55	2.1	9.2	20	0.7
North Long Beach	53	2.2	7.0	19	0.7
Riverside	52	1.6	6.0	42	0.6
Upland	54	1.8	9.0	30	0.7
BASIN AVERAGE:	56	2.0		25	0.7
SOUTH CENTRAL COAST AIR BASIN:					
Santa Barbara	46	1.9	21.0	50	0.5
Simi Valley	56	1.4	5.0	46	0.6
BASIN AVERAGE:	51	1.7		48	0.6
SAN DIEGO AIR BASIN:					
Chula Vista	56	1.8	12.0	39	0.6
El Cajon	50	1.5	5.0	46	0.6
BASIN AVERAGE:	53	1.7		42	0.6
NORTHERN CALIFORNIA SITES					
SAN FRANCISCO BAY AREA AIR BASIN:					
Concord	24	NA	2.0	75	NA
Fremont	26	1.6	7.0	50	0.5
Richmond	29	0.8	2.0	69	0.6
San Francisco	19	0.5	4.0	84	0.2
San Jose	28	1.1	4.0	57	0.6
BASIN AVERAGE:	25	1.0		66	0.5
SAN JOAQUIN VALLEY AIR BASIN:					
Bakersfield	30	1.6	6.0	43	0.6
Fresno	32	1.0	5.0	66	0.5
Merced	26	0.4	3.0	88	0.1
Modesto	28	0.5	3.0	86	0.2
Stockton	34	0.4	2.0	91	0.3
BASIN AVERAGE:	30	0.8		75	0.3
SACRAMENTO COUNTY[c]:					
Citrus Heights	31	0.5	3.0	87	0.2

a Gleit's method was used to estimate the concentration of samples below the quantitation limit. NA indicates the site data were not appropriate for the method and no value could be calculated.

b LOD is the limit of quantitation of the analysis method. The LOD for all samples is 1.0 part per billion.

c Since there is only one monitoring station located in the Sacramento Valley Air Basin, the concentration was estimated for Sacramento County.

the simulations reported in Gleit's paper show that his method is more accurate than other commonly used approximations. A detailed description of the method used to estimate the concentration of data below the LOD is provided in Appendix II.

The values for samples below the LOD estimated by this method range from 0.1 ppb to 0.8 ppb. The specific values for each station are shown in Table II-2. Note that as the percentage of samples above the LOD increases the estimated value for the samples below the LOD also increases. Gleit's method could not be applied to the data from the Concord station because the data above the LOD exhibit little or no variation, which is necessary for the application of the method.

The mean concentration for the monitoring stations ranges from 0.4 ppb at the Merced and Stockton sites to 2.5 ppb at the El Monte site. The mean concentrations of the data reported for each monitoring station are displayed in Table II-2. Mean concentrations calculated for the southern California stations are generally higher than those calculated for the northern California stations. The overall mean for the southern California stations is 1.9 ppb compared with 0.8 ppb for the northern California stations.

In addition to reporting the mean concentration for each monitoring station, Table II-2 also reports the peak 24-hour average concentrations. The peak concentrations range from 2.0 ppb at the Concord, Richmond, and Stockton stations to 21.0 ppb at the Santa Barbara station.

The observation that methylene chloride concentrations tend to be higher at southern California stations, particularly in the South Coast Air Basin (SCAB), is consistent with what is known about the uses and emissions of methylene chloride. First, the majority of the state's large methylene chloride emissions sources identified thus far are located in the SCAB. Second, about 40 percent of the state's population is located in the SCAB and since the amount of methylene chloride consumed for several use types is proportional to population, emissions from these uses would be expected to be concentrated in the SCAB. Therefore, the mean concentrations as well as the peak concentrations of methylene chloride are expected to be higher for stations in the SCAB. Chapter III of this report discusses the various categories for which methylene chloride is used as well as the annual emissions associated with each use.

Results from two short-term monitoring studies in the SCAB show concentrations of methylene chloride similar to ARB monitoring data. Based on two weeks of monitoring in 1979, the mean concentration of methylene chloride in Los Angeles was reported to be 3.8 ppb with the

maximum concentration reported to be 12 ppb (Singh, et al., 1981). Another study reports a mean concentration of 2.0 ppb with a maximum of 9.4 ppb for Riverside, based on 10 days of monitoring in 1980 (Singh, et al., 1982). The concentrations reported in these studies are consistent with the range of concentrations measured by the ARB in the SCAB. However, the results from these two studies are not sufficient to determine an annual average concentration of methylene chloride.

The methylene chloride monitoring data available for January 1985 through March 1987 at any one station represent only a small (2 to 8 percent) fraction of all days during the time period. Because of the limited number of samples, the high percentage of samples below the LOD, the variability in meteorology from year to year, and the unquantified error associated with the sampling and analysis procedure, there is some degree of uncertainty associated with assuming that the mean concentration of all data collected for each monitoring site is representative of an annual average. In an attempt to try to quantify this uncertainty we have calculated the upper and lower bound estimates of the mean concentrations which are intended to estimate the probable range of the annual average concentration at each monitoring station.

ARB staff developed a statistical treatment for calculating upper and lower bound estimates of the mean concentration at each monitoring station. This treatment provides an estimate of the uncertainty associated with the mean concentration. This method takes into account factors such as sample size, variance of the data, and an estimate of the uncertainty associated with the sampling and analysis procedure. The following text is a discussion of the statistical treatment used.

A scatter plot of the methylene chloride monitoring data indicates that they are distributed lognormally. Because available software only analyze data that are normally distributed, methylene chloride monitoring data were first converted from a lognormal distribution to a normal distribution. This was done by using the logarithms of the data for the analysis and then converting the results back to concentration units. The Statistical Analysis System (SAS, 1982) was used to calculate the standard error about the mean. The standard error calculated from the logarithms of the data are then converted back into concentration units. The upper and lower bound estimates reported for the mean represent two standard errors. Though the error in the sampling and analysis has not been determined, we assumed an overall uncertainty factor of $\pm$ 20 percent at one standard deviation to calculate the upper and lower bound estimates of the mean. The lower bound estimate represents two standard errors for the data with each sample concentration reduced by 20 percent. The upper bound estimate represents two standard errors for the data with each sample concentration increased by 20 percent. Upper and lower bound estimates for each station are shown in Table II-3.

TABLE II-3

RANGE OF ESTIMATED MEAN METHYLENE CHLORIDE CONCENTRATIONS FOR JANUARY 1985 THROUGH MARCH 1987[a] (units are parts per billion ppb)

Air Basin Site Location	Lower Bound Estimate	Estimated Mean	Upper Bound Estimate
SOUTH COAST AIR BASIN (SCAB):			
El Monte	1.8	2.5	3.5
Los Angeles	1.4	2.1	3.0
North Long Beach	1.5	2.2	3.2
Riverside	1.1	1.6	2.4
Upland	1.2	1.8	2.6
SOUTH CENTRAL COAST AIR BASIN (SCCAB):			
Santa Barbara	1.2	1.9	3.9
Simi Valley	0.9	1.4	1.9
SAN DIEGO AIR BASIN (SDAB):			
Chula Vista	1.2	1.8	2.7
El Cajon	1.0	1.5	2.2
SAN FRANCISCO BAY AREA AIR BASIN (SFBAAB):			
Concord	NA	NA	NA
Fremont	0.9	1.6	2.7
Richmond	0.6	0.8	1.2
San Francisco	0.3	0.5	1.0
San Jose	0.7	1.1	1.7
SAN JOAQUIN VALLEY AIR BASIN (SJVAB):			
Bakersfield	1.0	1.6	2.5
Fresno	0.6	1.0	1.4
Merced	0.2	0.4	0.6
Modesto	0.3	0.5	0.7
Stockton	0.3	0.4	0.5
SACRAMENTO COUNTY[b]:			
Citrus Heights	0.3	0.5	0.7

[a] Gleit's method was used to estimate the concentration of samples below the quantitation limit. NA indicates the site data were not appropriate for the method and no value could be calculated.

[b] Since there is only one monitoring station located in the Sacramento Valley Air Basin, the concentration was estimated for Sacramento County.

C. EXPOSURE IN CALIFORNIA

Population exposure in California for six areas (five air basins and one county) was estimated using the mean concentrations calculated for each monitoring station. The mean population exposure estimates for the SCAB and the San Francisco Bay Area Air Basin (SFBAAB) were estimated by interpolating station means to census tract centroids. For the other areas, a single estimated mean concentration was calculated, based on the means at monitoring stations in the area, and it was assumed that all the people in the area were exposed to this estimated mean concentration.

In order to present the possible range of exposure, upper and lower bound estimates of the mean were determined for each of the six areas. This required using the upper and lower bound estimates of the mean concentration for each monitoring station as presented in Table II-3. For the SCAB and SFBAAB the upper and lower bound estimates were calculated by the same method used to estimate the mean concentration. As for the other areas, the upper and lower bound estimates are simply the average of the station values. For each of the six areas, Table II-4 gives the mean, the upper and lower bound estimates of the mean, and the number of people exposed. The population residing in these six areas is approximately 20.3 million people which represents roughly eighty percent of California's population during 1985. Population estimates are based on 1980 census data projected to 1985.

The areas for which no monitoring data exist are predominantly rural areas. Generally, these areas are not densely populated nor are there many industrial sources. Thus, methylene chloride emissions, and consequently ambient concentrations are expected to be lower than those reported for the more urbanized areas listed in Table II-4. However, it is possible that people residing in the vicinity of methylene chloride emission sources could be exposed to higher concentrations.

Based on our analysis of the monitoring data, ARB staff estimate a population-weighted mean concentration of 2.2 ppb for over ten million people residing in the South Coast Air Basin. In the San Francisco Bay Area Air Basin the population-weighted mean concentration is 0.9 ppb for the Basin's 4.4 million residents. For all six areas studied, the mean annual methylene chloride concentration, weighted by population, is estimated to range from 1.1 to 2.4 ppb. Figure II-1 shows the statewide cumulative exposure to methylene chloride with upper and lower bound estimates of the mean.

TABLE II-4

RANGE OF ESTIMATED MEAN POPULATION-WEIGHTED
EXPOSURE ESTIMATES FOR JANUARY 1985 THROUGH MARCH 1987[a]
units are parts per billion (ppb)

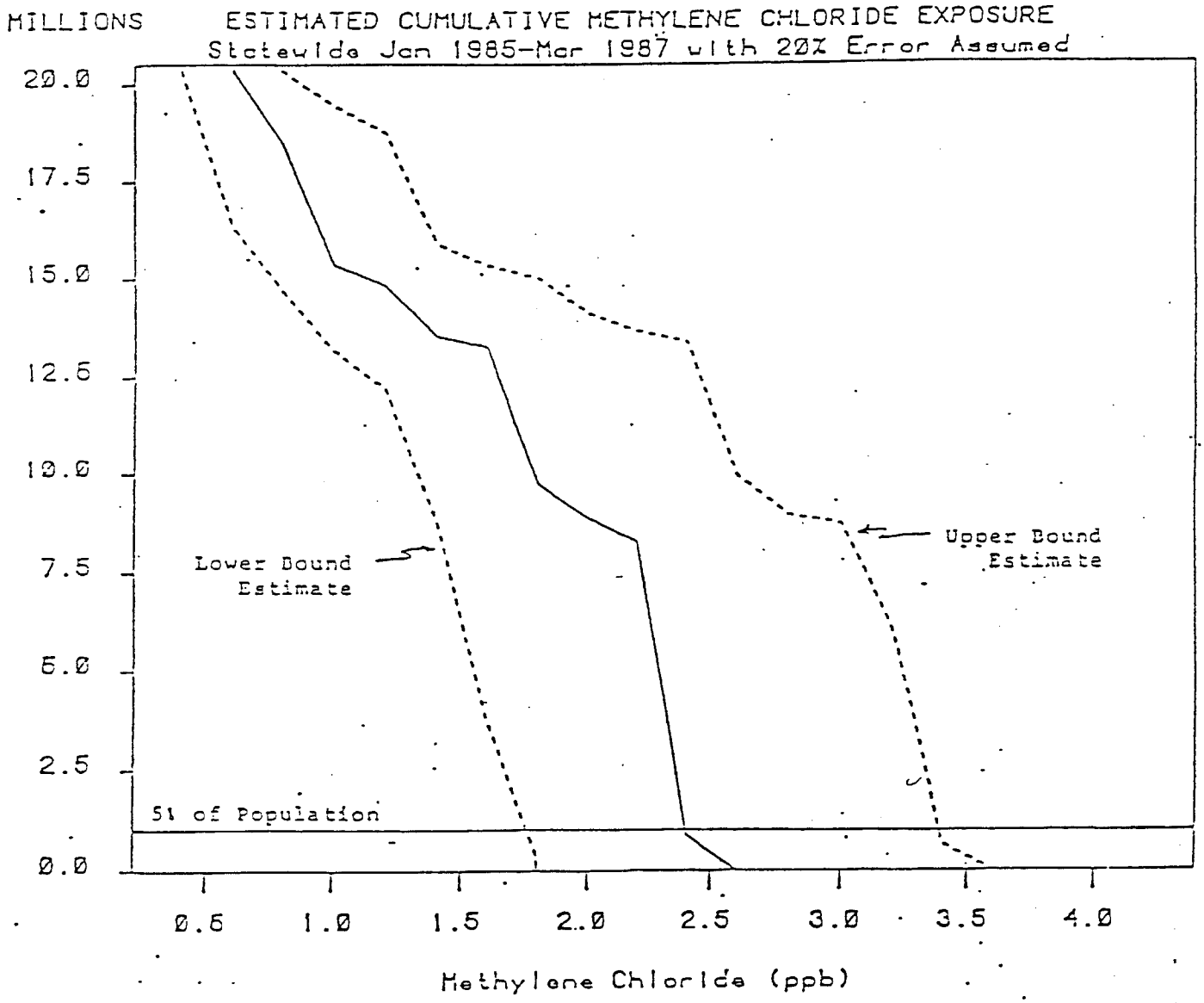
Air Basin	Lower Bound Estimate	Mean	Upper Bound Estimate	Population (millions)
South Coast[b]	1.5	2.2	3.1	10.09
San Francisco Bay Area[b]	0.6	0.9	1.6	4.39
San Diego	1.1	1.7	2.5	2.14
San Joaquin Valley	0.5	0.8	1.1	1.90
South Central Coast	1.1	1.7	2.5	0.92
Sacramento County	0.3	0.5	0.7	0.89
Overall Population-Weighted Average	1.1	1.6	2.4	20.33[c]

[a] Gleit's method was used to estimate the concentration of samples below the quantitation limit.

[b] The exposure estimates for the South Coast Air Basin and San Francisco Bay Area Air Basin are estimated by interpolating the mean concentrations at monitoring stations to census track centroids.

[c] Represents approximately 80 percent of California's population during 1985. The remaining 20 percent reside in areas in which no monitoring stations are located.

FIGURE II-1


MILLIONS
ESTIMATED CUMULATIVE METHYLENE CHLORIDE EXPOSURE
Statewide Jan 1985-Mar 1987 with 20% Error Assumed
20.0
17.5
15.0
12.5
10.0
7.5
5.0
2.5
0.0
Lower Bound Estimate
Upper Bound Estimate
5% of Population
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Methylene Chloride (ppb)

D. EXPOSURE NEAR EMISSION SOURCES

To assess the impact of methylene chloride emission sources on nearby populations, the ARB used emissions information in conjunction with meteorological data to estimate population exposure in census tracts surrounding three facilities that emit methylene chloride. The following text is a discussion of the data and modeling methodology used to estimate population exposure along with the exposure results.

The concentration estimates presented in this section do not represent the total ambient air exposure of the people living in the vicinity of the modeled sources. The concentrations reported are those which would exist if the modeled facility was the only methylene chloride emission source affecting the nearby population. In reality there are other emission sources, large and small, located in the basin which contribute to the total methylene chloride concentration that the modeled population is exposed to. The modeled population is expected to be exposed to ambient concentrations similar to those monitored by the toxic monitoring stations in the SCAB (1.5 to 3.1 ppb) which are additive to the concentrations solely due to the nearby modeled emission source. Other nearby sources, similar in both emissions and proximity, could produce additive concentrations on the order of those presented below.

The three facilities ARB modeled are located in the South Coast Air Basin (SCAB) and have annual emissions ranging from 52 to 587 tons. They are: Source A, a manufacturer of urethane foam; Source B, a motor home manufacturer which uses a methylene chloride containing adhesive; and Source C, an automobile assembler, which uses methylene chloride as a paint stripper. These facilities were chosen to model population exposure because they are large emission sources, their processes are typical of other SCAB sources and because they are located in densely populated areas.

For each facility, the Industrial Source Complex Short Term (ISCST) Gaussian model was used to predict the annual average concentration of methylene chloride in 1 square kilometer (km) cells for a 30 x 30 km grid. In addition, a 3 x 3 km grid of 0.01 km^2 cells was used to obtain a higher resolution of concentrations for the 1 km^2 cells nearest to the source. In order to predict the annual average concentration in each of the cells, the ISCST model requires emissions information and meteorological data as input for each facility.

Information on emissions was provided by each facility for the year 1985 in response to an ARB survey (CARB, 1986a). The information obtained for each facility includes emission rates, stack parameters, the typical operating schedule, and an estimate of the size of any area source. Annual emissions of methylene chloride from point and/or area

sources along with the stack height are given in Table II-5 for each facility that was modeled.

Point source emissions are typically released from specific stacks while area source emissions are released over a larger area. Source A and Source B have both point and area methylene chloride emission sources. The stack heights given for these two facilities refer to point source emissions. Although Source C emits methylene chloride from

TABLE II-5

ANNUAL EMISSIONS AND STACK HEIGHTS OF MODELED FACILITIES

Source	Point Source Emissions (tons/yr)	Stack Height (ft)	Area Source Emissions (tons/yr)
Source A	351.8	27	18.5
Source B	15.5	30	30.0
Source C	-	175	386.4

64 stacks, it was modeled as an area source with emissions released at an effective stack height of approximately 289 feet. This was determined to be appropriate due to the similarity in stack parameters and the relative closeness of the stacks, and because the emissions are released at ambient temperatures.

Meteorological data, as required by the ISCST model, were obtained from the nearest station to each facility. When more than one year of meteorological data were available, the year which yields the poorest pollutant dispersion was used. The meteorological data used to model Source C, Source A and Source B are from Los Angeles International Airport for 1978, Long Beach Airport for 1968, and Ontario Airport for 1972, respectively.

An annual average concentration is determined for each 1 square km cell (a total of 900 cells) in the grid surrounding each source. The modeled concentrations in each of the cells surrounding the source ranged from 0 to 1 ppb at Source C; from 0.01 to 10.8 ppb at Source A; and from 0 to 5.8 ppb at Source B.

Population exposure near each facility is determined by using the results from the ISCST model in conjunction with 1985 census data. The number of people living within each 1 square km cell in the modeled grid are exposed to the annual average concentration that was determined for

that cell. Additional methylene chloride emission sources in or near the modeled grid of each facility would increase the average population exposure. However, additional emission sources are not represented in this analysis.

Figures II-2 through II-4 show the cumulative population exposure for each facility. As shown in Figure II-2, approximately 1 million people are exposed to an annual average concentration of at least 0.10 ppb of methylene chloride resulting from Source A's emissions. Only concentrations less than 1 ppb are shown in Figures II-2 through II-4. Thus, the complete range in concentration for each facility is not shown.

The exposure results show that over 82,000 people are exposed to an annual average concentration of at least 0.5 ppb as a result of emissions from Source A. Of these 82,000, over 30,000 people are exposed to an annual average concentration of at least 1.0 ppb. More than 12,000 people are exposed to an annual average concentration of at least 0.5 ppb as a result of emissions from Source C, while more than 8,000 people are exposed to at least 0.5 ppb as a result of emissions from Source B. The modeling was also used to determine the population exposure in the 1 square km cell with the highest annual average concentration around each facility. For these cells, the annual average concentrations and the populations exposed are: 10.7 ppb/1,318 persons; 5.7 ppb/986 persons and 1.0 ppb/1,982 persons for Source A, Source B and Source C, respectively.

The modeling results demonstrate that several thousand people living near these facilities are exposed to methylene chloride at concentrations higher than annual average concentrations monitored in the SCAB. In addition, these results imply that other methylene chloride emission sources in California may expose nearby populations to elevated concentrations. In the SCAB there are 33 facilities with annual methylene chloride emissions of over 25 tons (SCAQMD, 1985). Of these 33 facilities, nine have annual emissions in excess of 100 tons.

To assess the impact these other facilities have on nearby populations requires facility specific information. The source with the greatest emissions does not necessarily produce the highest annual average concentrations in the surrounding area. This is apparent from the modeling results. The concentrations in the nearby community resulting from Source C's emissions are significantly lower than those produced by Source B, a facility with one-tenth Source C's annual emissions. This may in part be attributed to meteorology. However, the primary reason is the height at which emissions are released from Source C.

Figure II-2

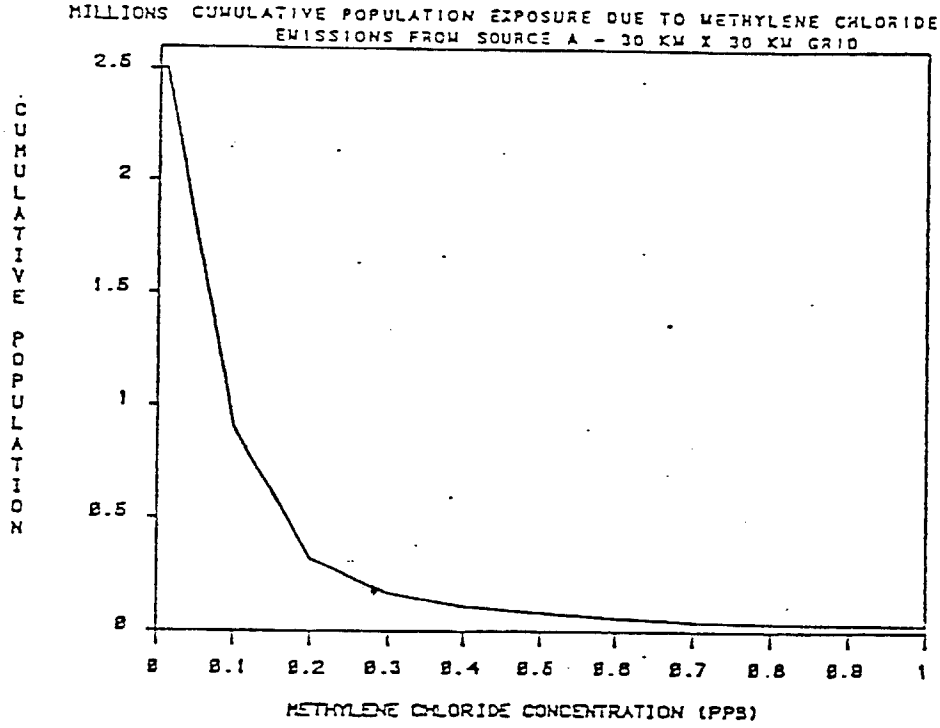


Figure II-3.

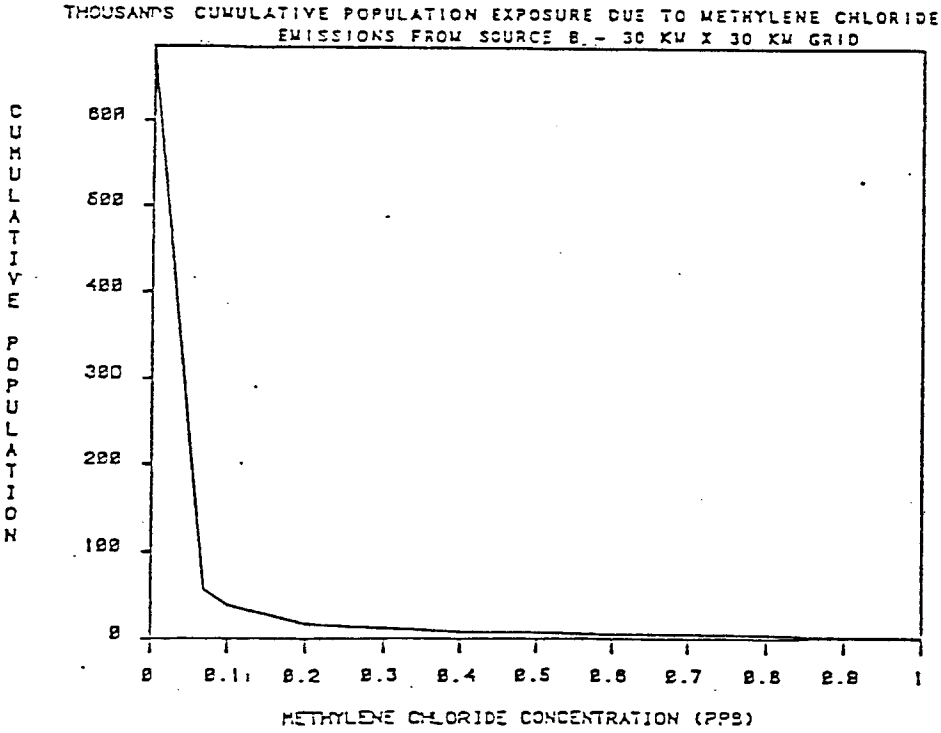
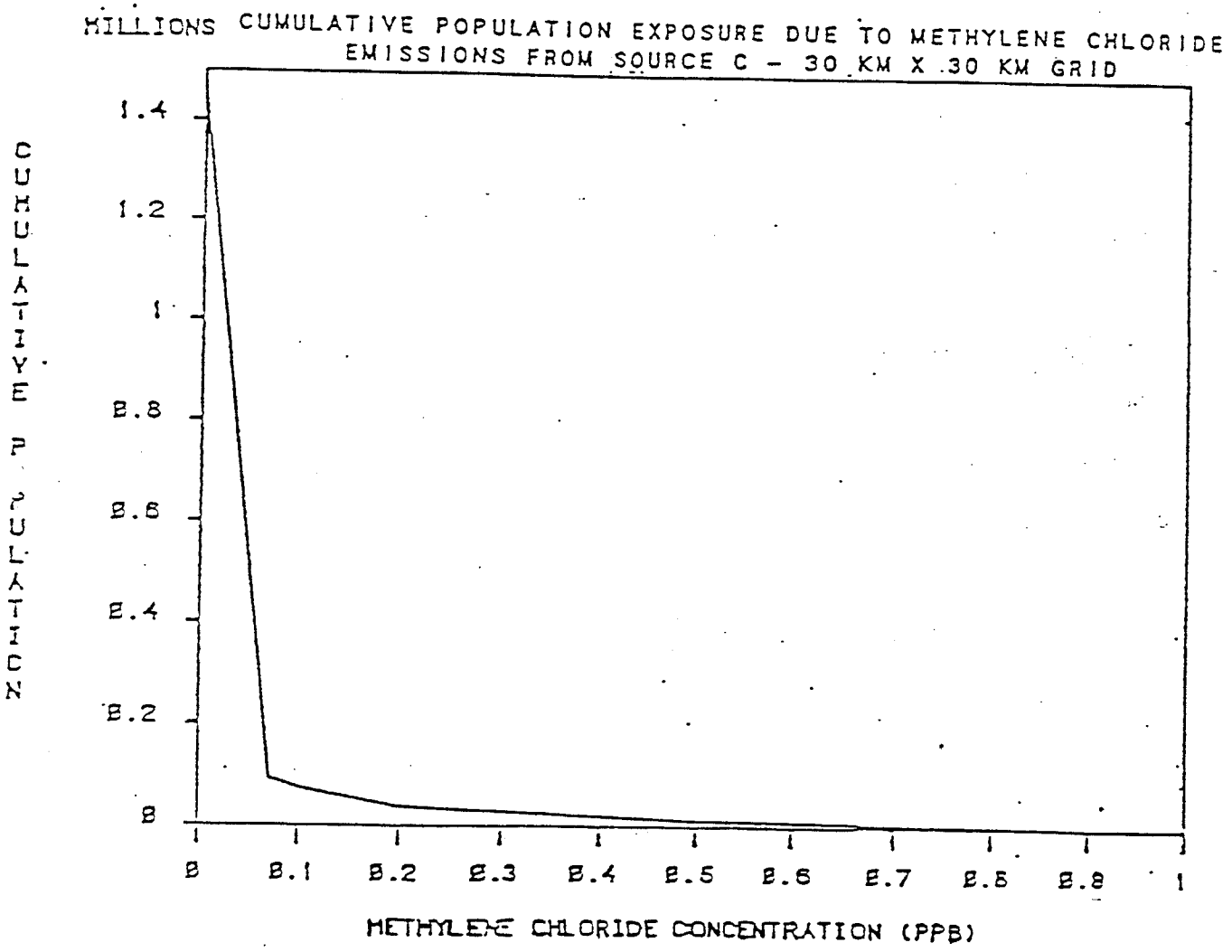


FIGURE II-4


MILLIONS CUMULATIVE POPULATION EXPOSURE DUE TO METHYLENE CHLORIDE EMISSIONS FROM SOURCE C - 30 KM X 30 KM GRID
CUMULATIVE POPULATION
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
METHYLENE CHLORIDE CONCENTRATION (PPB)

E. INDOOR EXPOSURE

An estimate of exposure to methylene chloride from indoor air is not provided in this section because the data necessary to make such an estimate are not available. However, because methylene chloride is a constituent in many household consumer products, indoor concentrations may be substantially higher than ambient concentrations. Inhalation of methylene chloride from the indoor environment is expected to vary depending on many factors including the degree and manner of use of products containing methylene chloride. This section presents information concerning what is known about indoor concentrations of methylene chloride as well as the levels of exposure that may occur from using products that contain methylene chloride. For methylene chloride it is reasonable to assume that ambient concentrations establish baseline indoor concentrations. Thus, any reduction in ambient levels of methylene chloride will also act to reduce indoor concentrations by a similar margin.

There are several studies that have monitored for indoor air pollutants. However, ARB staff are only aware of two indoor studies that have monitored for methylene chloride. A limited study, conducted in Italy, monitored the indoor air of 15 structures (nine houses, five apartments and one office) for several compounds including methylene chloride (De Bortoli, et al., 1985). Based on charcoal tube collection and gas chromatography (electron-capture detector) analysis, the mean indoor concentration of methylene chloride for all data from four to seven days of monitoring at each structure was 193 ppb with the indoor concentration for one of the structures reported as 1450 ppb. The mean outdoor concentration was reported as less than 4 ppb. Although the study is limited, the results show that indoor concentrations of methylene chloride can be many times higher than outdoor concentrations. This conclusion is supported by the National Research Council (NRC, 1978). When considering the significance of De Bortoli's findings to indoor exposure in California, it is necessary to note that building materials as well as consumer products used in Italy may differ from those used in California. For example, the peak concentrations reported in De Bortoli's study correlated with the use of hairsprays which contain methylene chloride, these products are no longer produced or sold in the United States. However, because a number of consumer products containing methylene chloride are used in California, it is likely that indoor concentrations of methylene chloride in some homes may be similar or greater to those reported by De Bortoli.

As part of a study conducted in Los Angeles County, the indoor and outdoor air of 51 homes during the winter season and 43 homes during the summer season was sampled and subsequently analyzed for several organic compounds (Pellizzari, et al., 1988). However, because Tenax is not an

effective media for collecting methylene chloride and because Tenax was used to collect the majority of the samples that were taken, methylene chloride results are only available for eight homes during the summer season. For these homes, draft results show overnight indoor concentrations (based on canister collection and mass spectrometer analysis) to range from 0.3 to 3.6 ppb with a mean concentration of 1.7 ppb while daytime indoor concentrations range from 0.3 to 3.9 ppb with a mean concentration of 1.6 ppb. Overnight outdoor concentrations range from 0.1 to 1.3 ppb with a mean outdoor concentration of 0.5 ppb while daytime outdoor concentrations range from 0.2 to 3.9 ppb with a mean concentration of 1.0 ppb. The results reported by Pellizzari et al. for methylene chloride are for a limited number of homes. However, they do indicate that indoor concentrations of methylene chloride in some homes may not be substantially higher than outdoor concentrations. Most likely, this is the case when products which contain methylene chloride are not used or stored indoors.

Because of the sampling and analysis methods used, ARB staff believe that the draft results from the Los Angeles study are more reliable than the results for the Italian study. However, the differences between the results for the two studies as well as the fact that both studies are very limited illustrates the need for a comprehensive indoor monitoring study where methylene chloride is sampled and analyzed throughout California. Such a study would provide the information needed to better characterize indoor exposure to methylene chloride in California.

Several studies have shown that personal breathing zone concentrations resulting from the use of consumer products containing methylene chloride may be several orders of magnitude higher than ambient concentrations. These products, which include spray paints and paint strippers, are used widely by the general population. Results from a chamber study where a paint stripper containing methylene chloride was being used show breathing zone exposures up to about 2,000 ppm averaged over one hour with peak concentrations as high as 3,300 ppm (Girman and Hodgson, 1986). For this study participants were placed in a chamber (20 meters^3) and supplied with a pressure demand breathing apparatus and therefore not exposed to elevated levels of methylene chloride. In another study, participants were placed in a chamber (5.4 meters^3) and requested to use personal-care-products containing methylene chloride. Peak use concentrations ranged from 95 to over 500 ppm and the fifteen minute time-weighted-average concentration was 102 ppm (Skory et al., 1975). The purpose of the study was to determine the participants levels of carboxy hemoglobin following normal use exposures to aerosol products containing methylene chloride. Otson et al. (1981) reported one hour time-weighted-average concentrations ranging from 37 to 1460 ppm as a result of paint stripper use in a chamber with a volume of approximately 28 meters^3. For this study, laboratory personnel

participants were supplied with respirators and thus were not exposed to elevated levels of methylene chloride. The purpose of the study was to evaluate air levels of methylene chloride generated by the use of small quantities of paint removers under poor ventilation conditions. Stevenson et al. (1978) reported a 26 minute average exposure of 450 ppm when test subjects placed in a chamber (approximately 75 meters^3) were exposed to methylene chloride through the use of aerosol spray paint. The purpose of this study was to determine airborne levels of methylene chloride and its effects on carboxy hemoglobin levels under simulated home-use conditions using typical commercial spray paint formulations.

Breathing zone concentrations of the magnitude reported above are generally found during the time period the product is being applied and can decline rapidly, depending on ventilation rate, once application is finished. Several factors are responsible for the range of results reported by these studies. These factors include: the concentration of methylene chloride in the consumer product used, the manner and duration of use, the volume of the study chamber, the ventilation rate of the study area, and the averaging time for the concentration reported.

The magnitude of exposures from the use of consumer products containing methylene chloride is put into perspective when the intake of methylene chloride from these exposures is compared to the intake from the ambient air. However, the following comparison is not intended to imply that the health effects associated with these two exposure scenarios are equivalent. The intake of methylene chloride from inhalation for approximately 20 minutes each year at a concentration of 100 ppm (Cal/OSHA's 8 hour time-weighted permissible exposure limit for methylene chloride) is equal to the annual intake from continuously breathing methylene chloride at a concentration of 2.0 ppb (the annual average concentration in the SCAB for January 1985 through March 1987). Exposure to methylene chloride from indoor air is an additional route of exposure and adds to the total risk.

Exposure to methylene chloride from the use of consumer products is expected to decline over the next several years. The reasons for the decrease are: 1) the FDA has proposed a rule to ban the use of methylene chloride as an ingredient of personal-care-products and, 2) the Consumer Product Safety Commission has announced that it will require certain consumer products which contain methylene chloride to be labelled in a manner which adequately describes the potential for chronic health effects. The labelling requirement is expected to cause manufacturers of these consumer products to switch to safer substitutes when available.

ARB staff did not make an estimate of the annual exposure to methylene chloride through use of consumer products. To do so would require detailed information on the manner and frequency with which methylene chloride containing products are used. Currently, there are

studies, both planned and underway, which may be helpful in evaluating indoor air exposure to methylene chloride.

The EPA in conjunction with the Consumer Product Safety Commission has conducted a survey on consumer use habits. The survey included responses from roughly 5,000 people about the incidence and frequency of their use of products, quantities used and typical protective measures taken. A solvent shelf survey was also conducted to analyze household products for the presence of chlorinated solvents including methylene chloride. The EPA plans to develop exposure estimates based on these surveys. ARB staff plan to review the results when they become available.

F. EXPOSURE THROUGH OTHER ROUTES

The primary focus of this report is to assess the adverse effects on health due to methylene chloride exposure in ambient air. In the six areas for which ambient monitoring data are available the population-weighted-average ambient concentration for 20.3 million people is estimated as 1.6 ppb. Based on this concentration and a breathing rate of 20 m^3/day, the population-weighted-average intake of methylene chloride through inhalation is 40,500 micrograms/year. For many California residents, nearby emission sources and indoor air contribute to additional exposure; resulting in even higher yearly intakes.

Exposure may also occur through the ingestion of methylene chloride, if present, in drinking water and food products. The following comparisons simply illustrate the extent of exposures to methylene chloride by routes other than inhalation. The comparisons do not imply that equivalent doses via different exposure routes necessarily result in health effects that are equivalent. ARB staff believe that the greatest contribution to total intake is from inhalation of methylene chloride.

The ARB staff estimate that for the majority of California residents, the intake of methylene chloride through drinking water is less than 365 ug/year. Between January, 1984 and December, 1985, the Department of Health Services conducted a study in which groundwater from 2,947 wells, representing 819 public water systems, was analyzed for methylene chloride. Less than one percent of the wells sampled (eleven wells) contained methylene chloride at concentrations above the 0.5 ug/liter detection limit. For these eleven wells the median concentration was 3.0 ug/liter, the maximum was 10.0 ug/liter and the minimum was 0.65 ug/liter (DHS, 1986).

Groundwater supplies roughly 40 percent of California's domestic use with surface water making up the other 60 percent. The DHS study did not monitor surface waters for methylene chloride. Methylene chloride released into surface waters is not expected to remain due to

its high volatility. The EPA used results from two major surveys (the National Organics Monitoring Survey and the National Screening Program for Organics in Drinking Water) to predict methylene chloride concentrations in the potable water of public water systems nationwide. Based on data from both groundwater and surface water, the EPA has estimated that 93.5 percent of the U.S. population who are served by public drinking water systems receive water with no methylene chloride or levels less than 0.5 ug/liter. Furthermore, 99.6 percent of the population receive water with concentrations at or below 10 ug/liter (U.S. EPA, 1984).

ARB staff estimated a range of annual intake through drinking water based on the concentrations found in the DHS monitoring study (less than 0.5 to 10.0 ug/liter). Intake is based on an average drinking water consumption of two liters per day, resulting in an intake ranging from less than 365 ug/year to 7300 ug/yr. Because methylene chloride is not expected to remain in surface waters and because methylene chloride was not detected in over 99 percent of the groundwater wells that DHS tested, ARB staff believe that the overwhelming majority of California population would have annual intakes less than those reported above.

Decaffeinated coffee was considered as a source of methylene chloride in food products. Because the United States population consumes a large volume of decaffeinated coffee that is manufactured using methylene chloride, the Food and Drug Administration (FDA) has estimated a maximum likely intake through this route. The FDA's food and color additive regulations limit the methylene chloride residual allowed in roasted and instant coffee to 10 ppm. To estimate upper-bound exposure, the FDA assumed that all decaffeinated coffee products contain methylene chloride at the maximum level allowed (10 ppm) and that all of it is extracted during brewing and becomes part of the beverage. Using information available on the average consumption of decaffeinated coffee, FDA estimated that the daily intake is not likely to exceed 140 micrograms (51,000 micrograms/year) due to ingestion of decaffeinated coffee (FR, 50(243): 51551).

The assumptions made by FDA were choosen so that the estimated intake represents a maximum which is not likely to be exceeded by consumers of decaffeinated coffee. Actual intakes are probably much lower for two reasons. First, most coffee products are not expected to contain methylene chloride at the maximum level allowed. One manufacturer, General Foods Corporation, found residuals of 0.10 ppm or less in 100 percent of 69 ground coffee samples and 54 instant coffee samples (FR, 50, (243): 51551). Second, all methylene chloride present in coffee may not be ingested with the beverage. Some residual may remain in coffee grounds and it is likely that methylene chloride which does enter the beverage may volatilize at the high temperatures experienced during brewing. The boiling point of methylene chloride is

40°C whereas coffee is brewed at temperatures near the boiling point of water, 100°C. However, all of the methylene chloride that volatilizes during brewing would be expected to enter the indoor environment and thus be available for inhalation by the residents.

The FDA is not aware of any possible public health hazards posed by the presence of methylene chloride in foods other than decaffeinated coffee.

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Otson, R.; Williams, D. T.; and Bothwell, P.D. 1981. "Dichloromethane Levels in Air After Application of Paint Removers" American Industrial Hygiene Association Journal Vol 42, pp. 56-60, 1981.

Pellizzari, E.D.; Michael, L.C.; Perritt, K.; Smith, D.J.; Hartwell, T.D.; Sebestik, J., 1988. "Comparison of Indoor and Outdoor Toxic Air Pollutant Levels in Several Southern California Communities", Draft Final Report, Contract Number: A5-174-33, Research Triangle Institute, Research Triangle Park, N.C.

Figure III-1

U.S. Production of Methylene Chloride

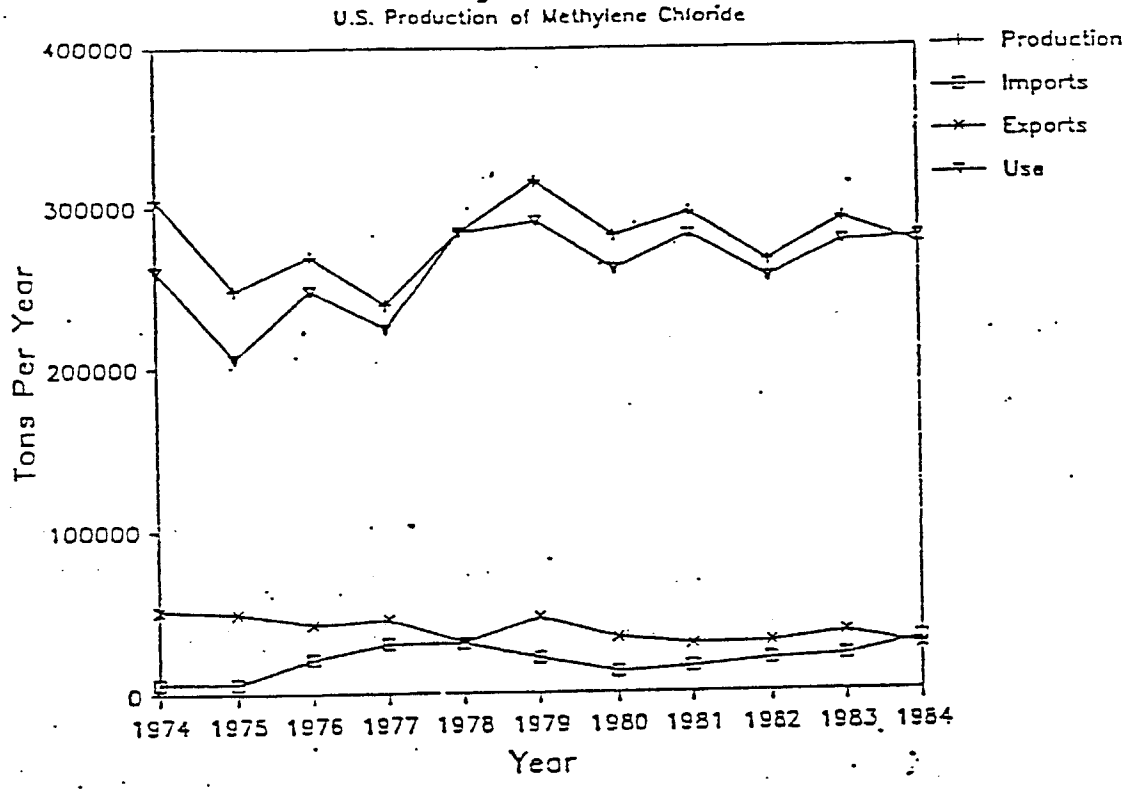
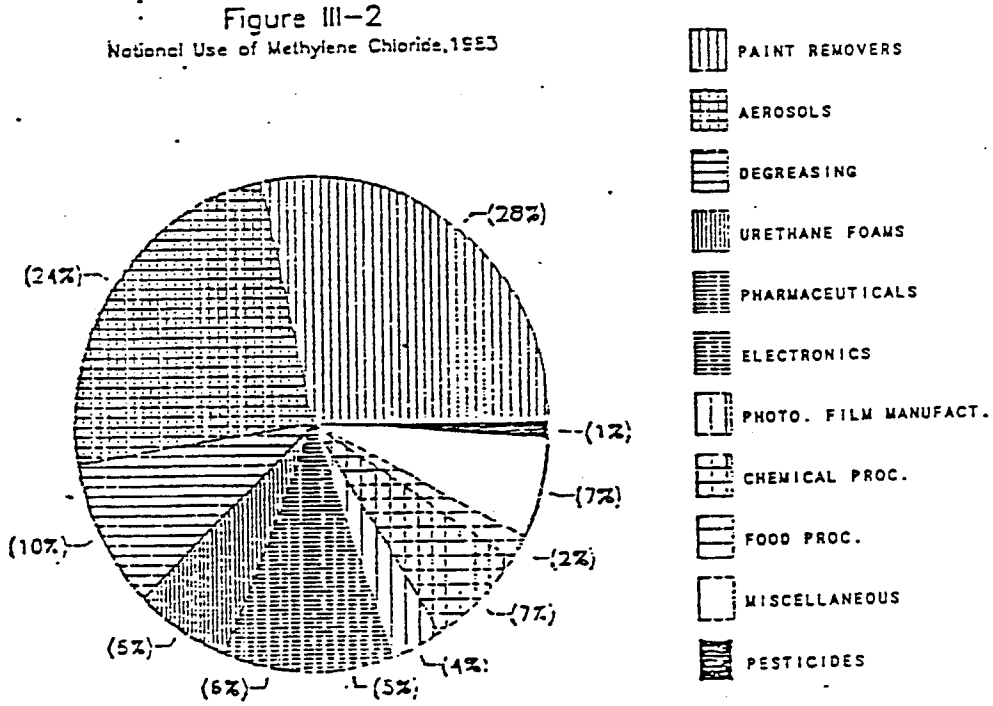


Figure III-2

National Use of Methylene Chloride, 1983



B. USES AND EMISSIONS

Methylene chloride is used in California in the following products and processes: paint removers, aerosols, foam manufacturing, degreasing operations, pesticide manufacturing, pesticide application, pharmaceutical manufacturing, food processing, and chemical production. Methylene chloride is also used in miscellaneous applications such as a thinning agent in adhesives, a solvent in surface coatings, a mold release agent in plastics manufacturing, and as a shrink fitting agent.

The Halogenated Solvents Industry Alliance (HSIA) supplied the ARB with data on the amounts of methylene chloride shipped to California by domestic manufacturers of the chemical (HSIA, 1986a). Data are presented below for the time period 1980 through 1985 (data for 1981 are not available).

Year	Domestic Manufacturers CH_2Cl_2 Shipments to California (tons)
1980	30,408
1981	NA
1982	25,054
1983	26,501
1984	23,123
1985	23,462

The shipping data submitted by HSIA do not account for several possible distribution alternatives:

(1) Accounts receiving shipments in California may reship portions of those shipments outside the state.
(2) Organizations other than domestic manufacturers may ship methylene chloride to California after purchasing it in another state. Such organizations may include chemical distributors, private companies who use the chemical, and military agencies.
(3) There may be a small fraction of California use which is imported from foreign methylene chloride producers.

These distribution alternatives are expected to represent a small fraction of total California use. Thus the figures supplied by HSIA are thought to be a good estimate of total California consumption.

Figure III-2 presents the percent of methylene chloride consumed in the U.S. by use type. Table III-1 presents the California and U.S. consumption of methylene chloride by use type in tons per year (TPY).

TABLE III-1

SUMMARY OF METHYLENE CHLORIDE USE (TPY)

Use Type	Estimated California Use[a]	Estimated United States Use[b]
Paint Removers	7,500	68,300
Aerosols	6,400	58,300
Degreasing	3,100	23,700
Urethane Foam Manufacturing	1,600[c]	15,600
Pharmaceuticals	500[d]	14,600
Electronics (Photoresist Stripping)	640[d]	13,100
Photographic Film Manufacturing	0	8,900
Specialty Chemical Production	800[d]	8,700
Chemical Processing Industry	1,200[d]	7,500
Food Processing	25[d]	3,700
Triacetate Fibers	0	2,600
Pesticide Manufacturing	800[e]	3,000
Miscellaneous	1,500	13,400
TOTAL USE[f]	24,000	241,000[g]

a. Appendix II describes the methods used to estimate California use. California use is based on information from 1983 unless otherwise noted.
b. All U.S. use is based on information from the Halogenated Solvents Industry Alliance for Calendar Year 1983. (HSIA, 1985)
c. Foam manufacturing use is based on 1984 emission estimates for eight slabstock foam plants identified by an EPA contractor (Pandullo and Nash, 1986a). This is does not include use for the manufacture of molded foam.
d. Use estimates for these categories are assumed to equal the amounts the domestic manufacturers reported shipping to California for these end-uses during 1985 (HSIA, 1986b). These are lower-end use estimates (See Appendix II).
e. Methylene chloride use in pesticide manufacturing includes only process use. It does not include methylene chloride consumed as an ingredient in pesticide formulations. Use information is for 1983.
f. Total use is rounded to the nearest 1000 TPY.
g. U.S. use for 1987 is estimated at 248,500 tons (HSIA, 1988).

The California use breakdown for methylene chloride as presented in Table III-1 is based on 1983 figures for all uses except urethane foam manufacture (1984 data), specialty chemical production (1985 data), the chemical processing industry (1985 data), food processing (1985 data), photoresist stripping (1985 data) and pharmaceutical manufacturing (1985 data). Discussion of the methodology used to estimate California consumption is included in Appendix II.

Emissions of methylene chloride in California result entirely from stationary sources and are estimated to be approximately 20,000 TPY. There is not sufficient information available to estimate emissions for several of the end uses listed in Table III-1. Additional emissions may result from sources that have not been identified in this report. Table III-2 presents the emissions by source type as well as the percentage of use that is expected to be emitted. Because methylene chloride is frequently used in a dispersive manner where few controls are in place, emissions of methylene chloride for several source types are assumed to equal 100 percent of its use.

Source types for which there are facilities in California with methylene chloride emissions greater than 100 TPY include: Foam manufacturing, paint stripping operations, degreasing operations, publicly owned treatment works, and hazardous waste landfills. Other source types that include facilities with emissions greater than 10 TPY include: paint remover formulators, pesticide manufacturing, chemical production, and possibly solvent reclaimers. Some facilities included as miscellaneous users may also emit substantial amounts of methylene chloride. Potential emission sources not evaluated include on-site solvent recovery and industrial waste water treatment. The following text discusses the various uses of methylene chloride as well as the emissions associated with each use when known.

Paint Removers

Paint removers account for the largest use of methylene chloride in California. An estimated 7,500 tons of methylene chloride were used in paint removers in California in 1983. Methylene chloride is the primary ingredient in paint stripping formulations used for industrial, commercial, military, and domestic applications. The majority of the methylene chloride in paint removers is used by the industrial sector. Factory and shop production for original equipment manufacture and after-market goods accounted for 70 percent of paint remover use in 1983 (Mullen and Mould, 1985).

In paint stripping applications, all of the methylene chloride used is eventually emitted to the atmosphere (U.S. EPA, 1985a). Thus, an estimated 7,500 tons of methylene chloride were emitted in 1983 from the formulation and use of paint removers. Emissions result from the use of

TABLE III-2

ESTIMATED EMISSIONS OF METHYLENE CHLORIDE IN CALIFORNIA[a]

Source	Emissions (TPY)	Percent of Use Emitted Percent	Reference
Paint Removers	7,500	100	U.S. EPA, 1985a
Aerosol Products	6,400	100	U.S. EPA, 1985a
Urethane Foam Manufacturing	1,600	100	U.S. EPA, 1985a
Degreasing Operations	2,600	83	U.S. EPA, 1985a
Pesticide Manufacturing	90	ND[b]	-
Chemical Production and Processing	57	Small Percent	U.S. EPA, 1985a
Distribution Facilities	11	0.2	U.S. EPA, 1985a
Solvent Reclamation	35	1-2	(O'Morrow, 1986; Schneider, 1986)
POTWs	225	ND	ARB, 1987
Photoresist Stripping	360	57	U.S. EPA, 1985a
Miscellaneous Uses	1,500	100	U.S. EPA, 1985a
Total Emissions[c]	20,000		

a. Emission estimates are for 1983 for all source categories except urethane foam manufacturing and pesticide manufacturing (1984 data), solvent reclamation (1985 data), photoresist stripping (1985 data), and POTWs (1987 data). Data on total emissions were not available for pharmaceutical manufacturing, food processing, specialty chemical production, the chemical process industry, pesticide application, municipal landfills, surface impoundments, and hazardous waste landfills.

b. ND - not determined.

c. Total emission estimate is rounded to the nearest 1000 TPY.

paint removers as well as from paint remover formulation facilities. Some paint removal operations emit greater than 100 TPY of methylene chloride to the atmosphere (Taback, et al., 1983). Methylene chloride is also emitted at paint remover formulation facilities during mixing, packaging, and storage (U.S. EPA, 1985a). It is estimated that there are seven paint remover formulation facilities in California with emissions estimated to equal 0.1 percent of use (PEI Assoc. Inc., 1985).

Aerosols

Aerosol products have historically been one of the largest uses of methylene chloride in California. California use of methylene chloride in 1983 was an estimated 6,400 tons. Use of methylene chloride in aerosol products throughout the U.S. appears to be decreasing in 1986; however, summary data are not available (Wind, 1986; Chemical Marketing Reporter, 1986). In response to a proposed FDA ban on the use of methylene chloride in aerosol cosmetics, most manufacturers of aerosol cosmetics (primarily hairsprays) stopped using methylene chloride in their products during 1986 (Wind, 1986).

Methylene chloride is used in aerosols as a solvent, a flammability suppresser, vapor pressure depressant, and viscosity thinner. It is used in hair sprays, paints, insecticides, cleaners, room deodorants, and various household and personal care products. The percentage of methylene chloride in the total aerosol formulation depends on what the product is. Aerosol paint strippers may contain as much as 85% methylene chloride. Aerosol products are packaged at central facilities before being distributed. Aerosols are largely consumer products. Thus, use and emissions are assumed to be distributed with population.

Aerosol packing and product use resulted in estimated emissions of 6,400 tons in California in 1983. Methylene chloride is emitted from aerosol products during the volatilization of suspended droplets or by evaporation from sprayed surfaces. All methylene chloride used in aerosol products is assumed to be emitted to the atmosphere (U.S. EPA, 1985a). Emissions also occur at aerosol packaging plants during spills, mixing, and aerosol can charging (PEI Assoc. Inc., 1985). There are at least 20 aerosol packaging plants in California (Johnson, 1982; Verhagen, 1984).

Foam Manufacturing

An estimated 1,600 tons of methylene chloride were used for manufacturing slabstock polyurethane foam in California in 1984 (Pandullo and Nash, 1986a). Methylene chloride is used in the manufacture of two types of foam products, slabstock and molded. Methylene chloride is used in different ways in these two processes. In

the slabstock foam manufacturing process, methylene chloride is used as a foam blowing agent. Methylene chloride, mixed with other ingredients, is discharged into a foam tunnel in which an exothermic reaction vaporizes the methylene chloride, forming air cells in the foam. In molded foam manufacture methylene chloride is used as a cleanup solvent (Pandullo and Nash, 1986a).

Methylene chloride is emitted from both slabstock and molded foam manufacturing processes. Mass balance data from manufacturers of slabstock foam indicate that about 60 percent of the initial charge of methylene chloride is emitted from the tunnel and about 40 percent from ventilation of the foam curing area (Pandullo and Nash, 1986a). Methylene chloride emissions from foam manufacturing plants are typically uncontrolled. Thus, all of the methylene chloride used in the process is emitted to the atmosphere (U.S. EPA, 1985a). An EPA contractor estimated emissions from eight slabstock foam manufacturing facilities in California in 1984 as 1,600 tons (Pandullo and Nash, 1986a). The majority of the identified emissions of methylene chloride from its use as a foam blowing agent are in the South Coast Air Basin. The number of molded foam manufacturing facilities in California and the methylene chloride emissions from such facilities have not been determined.

Degreasing Operations

Methylene chloride is also used in degreasing operations in California. California use of methylene chloride for degreasing was an estimated 3,100 tons in 1983. Degreasing is an integral part of many metal fabrication processes such as the manufacture of automobiles, electronics, furniture, appliances, jewelry, and plumbing fixtures. Methylene chloride is also used as a degreaser to a minor extent in the textile, paper, plastic, and glass manufacturing industries. Cold cleaning units account for 96 percent of all degreasers in the U.S. (PEI Assoc. Inc., 1985). An estimated 77 percent of the methylene chloride used as a degreasing solvent in the U.S. is used in cold cleaning units (PEI Assoc. Inc., 1985). Substantial quantities of the methylene chloride used for degreasing are sent to solvent reclaimers (U.S. EPA, 1985a).

Emissions of methylene chloride from degreasing operations in California are estimated as 2,600 tons for 1983. Approximately 83 percent of the fresh methylene chloride used for degreasing operations is emitted. This percentage estimate includes a weighted average emission factor for cold cleaning, conveyor and vapor degreasers and takes into account the emissions resulting from solvent returned to the degreasing operation from solvent reclaimers (U.S. EPA, 1985a; PEI Assoc. Inc., 1985; U.S. EPA, 1977). In this approach,

it is assumed that all solvent not consumed at the degreasing facility is sent to solvent reclaimers (U.S. EPA, 1985a). There are estimated to be several thousand cold cleaning facilities in California (Federal Register, 1985; PEI Assoc. Inc.,1985). The methylene chloride emissions for the average facility are 0.3 TPY (PEI Assoc. Inc., 1985). In addition, there are estimated to be over 100 facilities with vapor degreasers, with average methylene chloride emissions of 2.4 TPY per plant (PEI Assoc. Inc., 1985).

Pesticide Manufacturing

Methylene chloride is used as a solvent in some pesticide manufacturing processes. An EPA report lists the methylene chloride consumed by one pesticide manufacturing facility in California as 800 tons in 1983. This estimate includes only process use, and excludes that which may be added to pesticide formulations as an active or inert ingredient. No other pesticide manufacturing facilities in California that use methylene chloride have been identified.

Methylene chloride is used for extraction, phase separation, purification, crystallization, and as a general transport solvent (U.S. EPA, 1985a). The pesticide industry employs a variety of unit operations similar to those used in the chemical processing industry. Emissions of methylene chloride from the pesticide manufacturing facility identified above are estimated at 90 tons for 1984. The facility has reported that methylene chloride emissions from one process vent are controlled through incineration. (Pandullo and Nash, 1986b). Additional methylene chloride emissions from other pesticide manufacturing facilities in California may exist. However, staff of the EPA contractor researching this source category believes that most of the emissions have been identified (Pandullo, 1986c).

Chemical Processing and Specialty Chemical Production

Two facilities in California that use methylene chloride in chemical production have been identified. Based on information from an EPA contractor, one facility uses methylene chloride in the production of a specialty chemical (Howle, 1986) while the other uses methylene chloride in the production of rubber cement (U.S. EPA, 1985a). However, the total amount of methylene chloride used at these facilities is not known.

Emissions of methylene chloride from the production of rubber cement are estimated as 3 TPY (U.S. EPA 1985a). Emissions from the specialty chemical production facility are estimated as 54 TPY (Howle, 1986). These emissions are primarily from equipment leaks, equipment openings, and process vents. The staff is unaware of additional methylene chloride used by other chemical processing and production facilities in California.

Photoresist Stripping

In 1983 five percent of the methylene chloride consumed in the United States was used as a photoresist stripping solvent. Photoresist stripping occurs during the manufacture of copper clad laminated circuit boards. Recent information from electronics industry personnel and suppliers of photoresist films indicates a trend away from organic-solvent stripping has been occurring over the past few years (Waterhouse, 1986; ARB Survey 1986). The trend appears to be more pronounced in California than in the rest of the country.

Aqueous photoresist films which use alkaline stripping solution have gained popularity due to concerns about exposure to organic solvents. However, some methylene chloride based stripping is expected to continue for application to circuit boards requiring high resolution. Industry sources have stated that organic solvents must be used to meet the specifications of some military contracts (Rameriz, 1986; Waterhouse, 1986).

Emissions from photoresist stripping in California were estimated as 360 tons for calendar year 1985. This estimate is based on the assumption that total use for this category is equivalent to 640 tons, the HSIA's estimate of methylene chloride shipments to the electronics industry. An emission factor reported by EPA (1985a) was applied to this use estimate. There is some uncertainty as to whether this estimate is representative of current emissions due to shifting technology in the circuit board manufacturing industry.

Chemical Distributors

Virtually all methylene chloride produced is sold by chemical distributors. Distribution operations involve transport, storage, and repackaging of methylene chloride. There are estimated to be 500 regional distribution facilities in the U.S. (U.S. EPA, 1985a). An estimated 25,000 TPY of methylene chloride are sold through distribution facilities in California. California distribution was estimated as U.S. distribution times the ratio of the quantity of methylene chloride used in California to that used in the U.S.

Emissions of methylene chloride from distribution facilities in California were estimated to be 50 tons in 1983. Emissions resulting from storage tanks were calculated using assumptions about the throughput of methylene chloride and the number and size of storage tanks (U.S. EPA, 1985a; U.S. EPA, 1985b). Estimated emissions are 0.2 percent of the methylene chloride that is distributed.

Solvent Reclaimers

There are about 20 commercial solvent reclaimers in California. The largest three reclaimers handle 85 percent of the business (DHS, 1986). The largest of these accounts for almost half of the off-site solvent recovery in California. It is estimated that 2,400 tons of methylene chloride were sent for recycling in California in 1985. The quantity of methylene chloride sent for recycling in California was estimated by using: 1) the quantity of halogenated solvent reported on hazardous waste manifests (PEI Assoc. Inc., 1985), and 2) the estimated percent of methylene chloride contained in the halogenated solvents (O'Morrow, 1986; Schneider, 1986).

It is estimated that 35 ($\pm$ 15) tons of methylene chloride were emitted from solvent reclamation facilities in California during 1983. Most emissions result from storage and handling of waste and reclaimed solvents, although some emissions come from distillation condensers at reclamation facilities. Industry representatives estimated emission losses for a solvent as volatile as methylene chloride to be one to two percent of the methylene chloride received (O'Morrow, 1986; Schneider, 1986). Assuming that facility emissions are proportional to the throughput of solvents, the largest solvent reclaimer in the State may emit as much as 25 TPY of methylene chloride (McCormack, 1985).

Miscellaneous Uses

Miscellaneous use of methylene chloride in California was estimated to be 1,500 tons. Examples of miscellaneous uses of methylene chloride include: 1) a solvent for cleaning ink from printing equipment and as a thinning agent in some ink formations, 2) a solvent to bond plastic pieces together, 3) a thinning agent for adhesives, 4) a constituent in specialty cleaners, 5) a solvent for coatings where a fast-drying time is required, as for traffic paints, and 6) a constituent in photographic film cement. The magnitude of methylene chloride used and the resulting emissions for each of these individual applications has not been determined. Miscellaneous use is primarily dispersive and thus 100 percent of use is assumed to be emitted to the atmosphere.

C. SOURCES WITH UNQUANTIFIED EMISSIONS

Pesticide Application

Approximately 14 pesticidal products registered with the U.S. government contain methylene chloride as an active ingredient, and more than 1,750 registered pesticidal products contain methylene chloride as an inert ingredient (Federal Register, 1985). The quantity of methylene chloride applied in California as an active pesticidal ingredient was

minor in 1984 (less than 0.2 tons) (CDFA, 1984). The quantity of methylene chloride used in California as an inert ingredient in pesticides has not been determined.

Pharmaceutical Manufacturing

Methylene chloride is used in California in pharmaceutical manufacturing. Use is estimated as 500 tons in 1985 (HSIA, 1986b). Methylene chloride is used in pharmaceutical manufacturing in the U.S. in the following ways: as an extraction solvent and reaction media in production of bulk pharmaceutical chemicals, and as a carrier for tablet coatings such as cellulose ether films. The one pharmaceutical production facility in California identified by the EPA as using methylene chloride closed production operations in May 1985 (Blanchard, 1985; Pandullo, 1986a). Methylene chloride may be used in tablet coating operations at pharmaceutical manufacturing facilities in the State, although an EPA contractor assumed such usage to be small (Pandullo, 1986a; White, 1986). Emissions of methylene chloride from pharmaceutical manufacturing are probably small, based on information from an EPA contractor studying methylene chloride. The number of pharmaceutical manufacturing facilities in California that use methylene chloride was not determined.

Food Processing

Methylene chloride is used to extract heat sensitive substances such as caffeine, cocoa, hops, and edible fats (U.S. EPA, 1985a; HSIA, no date). For 1985, use of methylene chloride in food processing is estimated at 25 tons (HSIA, 1986b). Based on the available information at least two food processing facilities in California use methylene chloride. These facilities use methylene chloride as an extraction solvent for decaffeination of coffee (Hall, 1986).

Methylene chloride emissions from food processing operations in California were not determined. However, the majority of emissions are expected from the extraction process, and from storage and handling facilities (U.S. EPA, 1985a). Two coffee decaffeination facilities in California were identified (Hall, 1986). There may be other food processors with methylene chloride emissions. However, none have been identified.

POTWS and Landfills

In addition to the uses discussed above, methylene chloride may be released from municipal waste water treatment facilities, known as publicly owned treatment works (POTWs), municipal landfills, surface impoundments, and hazardous waste landfills. Methylene chloride emitted

from landfills and POTWs originates as waste streams from source types listed in Table III-1. For several source types emissions have been estimated as 100 percent of use. Thus, a portion of the emissions attributed to these source types may actually be released to the air at POTWs and landfills.

The quantities of methylene chloride that are disposed at municipal landfills throughout California have not been determined. None of the information reviewed for this report indicated the quantities of methylene chloride that are disposed of at municipal landfills. Although industrial wastes contaminated with methylene chloride can not be legally disposed in municipal landfills, the chemical inadvertently enters landfills as residues in consumer products such as aerosol cans and paint remover containers. In California, there are approximately 1,000 active and 1,200 inactive municipal landfills (Barnickol, 1986).

Hazardous waste landfills and surface impoundments may handle large quantities of methylene chloride. At least 1,500 tons of halogenated solvent containing wastes were disposed in landfills and at least 3,200 tons of halogenated solvent containing wastes were disposed at surface impoundments in California in 1985 (DHS, 1986).

In response to the Resource Conservation and Recovery Act, the Environmental Protection Agency is promulgating restrictions on land disposal of hazardous wastes. Effective November 8, 1986, spent solvent wastes are prohibited from land disposal. As detailed in the federal register (FR 50 (216): 40572) land disposal of solvent wastes which meet listed requirements will be allowed until November 8, 1988. Between November 1988 and November 1990 exemptions can be requested on a case by case basis. Beyond November 1990 no land disposal of solvent wastes is allowed.

In the past, fewer restrictions were placed on the land disposal of halogenated solvents, and the amounts disposed could have been greater. Methylene chloride previously disposed at closed and existing landfills escapes into the atmosphere over a period of several decades (U.S. EPA, 1986). The HSIA estimated that roughly 15 percent of the methylene chloride shipped to California ends up being disposed of by incineration or landfilling (HSIA, 1986a).

In response to AB 3374 all active disposal sites (municipal and hazardous waste) are required to conduct tests to determine: (1) the composition of landfill gases; (2) the presence of specified air contaminants in the ambient air at the disposal site perimeter; (3) whether or not off-site subsurface migration of landfill gas is occurring. Disposal site operators are required to report test results to the air pollution control officer by July 1, 1987 with the

possibility of an extension up to January 1, 1989. Methylene chloride is specified as one of the compounds for which testing will be performed. The test results should be useful in determining which disposal sites in the state may pose a potential public health risk.

POTWs are another source of methylene chloride emissions. Available information indicates that POTWs may be significant emission sources of methylene chloride. The Association of Bay Area Governments has estimated that the three major POTWs in Santa Clara County emit 44 TPY of methylene chloride (Hinman, et al., 1985). The largest POTW in the County was estimated to emit 26 TPY of methylene chloride. A more recent study estimates emissions of methylene chloride from POTWs in California to be 225 tons. For one facility in Los Angeles, emissions of methylene chloride were estimated to be 121 TPY (ARB, 1987). Methylene chloride is also emitted in route to POTWs at pump stations and at high points in the sewer line venting through manhole covers (Caulkins, 1986). Discharges of methylene chloride to POTWs are assumed to result primarily from industrial sources.

D. EMISSION TRENDS

Emissions of methylene chloride are expected to decline over the next few years as a result of a decline in use. Estimated production of methylene chloride in 1985 was down 10 to 15 percent from 1984. The demand for methylene chloride was forecasted to remain nearly stagnant in 1986 (Chemical and Engineering News, 1985). National consumption data for methylene chloride show a thirteen percent reduction from 286,100 tons in 1985 to 247,400 tons in 1987 (HSIA, 1988). Currently, we do not have any information which suggests that a similar reduction in consumption has not occurred in California. The decline in use for most of the source types are based on concerns about the health impacts of methylene chloride and the potential for governmental regulation (Chemical and Engineering News, 1985b; Wind, 1986; Chemical Marketing Reporter, 1986; Smart and Landels, 1985).

The emission trend for methylene chloride used as a paint remover is uncertain. The Consumer Products Safety Commission (CPSC) has determined that there are no good substitutes for methylene chloride in paint removers. The CPSC voted to institute rule making in February, 1986, which requires consumer products containing methylene chloride that are packaged after September 14, 1988 to comply with additional labeling requirements.

Declines in the use of methylene chloride in personal care products as well as spray paints have occured. The Federal Food and Drug Administration (FDA) has issued a notice of proposed rule making to ban methylene chloride in personal care products (Vogel, 1985). According

to the FDA as well as industry representatives, methylene chloride is not currently used in personal care products in the United States. The paint industry is also working to reformulate aerosol spray paints without methylene chloride (Chemical Marketing Reporter, 1986). National consumption data show that there has been a fourty six percent decline in the consumption of methylene chloride for use in aerosols from 1985 to 1987 (HSIA, 1988). This decline in consumption is expected to continue as suitable substitutes are identified.

The shift to less metal processing in producing automobiles and other durable goods tends to reduce the demand for the use of methylene chloride in industrial cleaners and degreasers. A slight decline is expected in the emissions of methylene chloride from pesticide manufacturing. This may result as 1,1,1-trichloroethane and other solvents are substituted for methylene chloride because of concern about health effects (Smart and Landels, 1985). The trend in emissions of methylene chloride in food processing is uncertain. EPA has determined that there is not sufficient justification to ban the chemical from use in decaffeinating coffee (Chemical Marketing Reporter, 1986).

Despite the expected decline in overall methylene chloride emissions, governmental regulation could cause an increase in methylene chloride emissions from some source types. Efforts to control methylene chloride residuals in waste water effluent might result in increased emissions from pharmaceutical manufacturing, POTWs, and solvent reclamation. EPA is currently seeking comment on the use of steam stripping technology for the removal of methylene chloride from pharmaceutical manufacturing waste waters (Federal Register, 1985). Steam stripping is an effective method of removing volatile organics such as methylene chloride by releasing them to the atmosphere. EPA is also considering approval of the use of steam stripping at POTWs to remove volatile organics (Federal Register, 1985). One reference estimated that about ten percent of the total methylene chloride used in the U.S. is released to water (Cothern, et al., 1984).

Methylene chloride emissions from solvent reclamation may also increase in the future. The quantities of methylene chloride received by solvent reclaimers have increased over the past few years and the trend may continue. Concerns about land disposal of halogenated solvents have prompted much of this trend.

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IV.

PROPERTIES AND ATMOSPHERIC FATE

A. PROPERTIES OF METHYLENE CHLORIDE

Methylene chloride (dichloromethane, DCM) is a nonflammable volatile liquid that is completely miscible with a variety of solvents (Anthony, 1979). In the absence of moisture, at ordinary temperatures, methylene chloride is relatively stable. In dry air, methylene chloride decomposes at temperatures exceeding 120°C. Methylene chloride evaporates relatively quickly from water. Selected properties of methylene chloride are given in Table IV-1.

TABLE IV-1

PHYSICAL PROPERTIES OF METHYLENE CHLORIDE

Properties	Value	References
Molecular Weight	84.94	U.S. EPA, 1982
Boiling Point (760 mmHg)	40°C	U.S. EPA, 1982
Melting Point	-95°C to -97°C	U.S. EPA, 1982
Vapor Pressure, 20°C	349 mm Hg	U.S. EPA, 1982
Solubility in H_2O, 20°C	20 g/liter	U.S. EPA, 1982
Density, 20°C	1.33 g/ml	WHO, 1984
Log Octanol/H_2O Partition Coeff.	1.25	WHO, 1984
Relative Evaporative Rate	14 (water = 1)	U.S. EPA, 1982
Color	Colorless	WHO, 1984
Odor	Ethereal	WHO, 1984
Flash Point	none	U.S. EPA, 1982

B. ATMOSPHERIC FATE

Reaction with hydroxyl radicals is the dominant mechanism removing methylene chloride from the troposphere. Estimates provided in the literature for methylene chloride's tropospheric lifetime range from 27 to 559 days. However, for reasons provided later in this Section, we believe that a range of 80 to 250 days is representative of typical atmospheric conditions. The rate at which this reaction proceeds depends on temperature and the tropospheric concentrations of both methylene chloride and hydroxyl radical. The temperature dependence of the reaction rate is incorporated in the rate constant for the reaction of CH_2Cl_2 with hydroxyl radical. The product of the rate constant and both species concentrations gives the rate at which methylene chloride is being degraded (Finlayson-Pitts and Pitts, 1986).

The tropospheric lifetime of a compound is an estimate of the time required for a given amount of the compound to decrease to 1/e (0.368) of its original value (at time zero). The tropospheric lifetime (τ) of methylene chloride is related to the rate constant (k) and the hydroxyl radical concentration ([.OH]) by the equation:

$$\tau = (k[.OH])^{-1} \qquad (1)$$

In deriving the above equation, it is assumed that hydroxyl radical is at a constant or steady state concentration in the troposphere.

ARB staff reviewed the literature published in the last ten years to obtain pertinent data on the rate of reaction of methylene chloride with the hydroxyl radical. We found five research groups that determined reaction rate constants from empirical data in the laboratory (Jeong & Kaufman, 1982; Howard & Evenson, 1976; Perry, et al., 1976; Davis, et al., 1976; Cox, et al., 1976). Other researcher's have used the data from one or more of these studies to estimate the tropospheric lifetime of methylene chloride.

Table IV-2 is a summary of the rate constant and tropospheric lifetime estimates resulting from our literature search. The table includes a temperature dependent expression for the rate constant and the room temperature rate constant. Also included in the table are the authors' estimates of tropospheric lifetime and the average tropospheric values of temperature and hydroxyl radical concentration.

The estimates of hydroxyl radical concentration and tropospheric temperature are responsible for much of the variation in the estimated tropospheric lifetimes. Because there is no clear agreement on the value of these parameters, we used a range for each to develop a range of atmospheric lifetime estimates.

TABLE IV-2

TROPOSPHERIC LIFETIME ESTIMATES AND RATE CONSTANT ESTIMATES
FOR METHYLENE CHLORIDE'S REACTION WITH HYDROXYL RADICALS

Temperature Dependent Rate Expression for the Hydroxyl Radical Reaction (cm^3/molecule.sec)	Room Temperature Rate Constant for the Hydroxyl Radical Reaction (10^{-14} cm^3/molecule.sec)	Atmospheric Lifetime (Days)	Average Tropospheric Values Used to Calculate Lifetime: Hydroxyl Concentration ($molecules/cm^3$)	Average Tropospheric Values Used to Calculate Lifetime: Temperature (Kelvin)	References
$8.54\ ^{+8.18}_{-4.18}) \times 10^{-18} T^2 \exp(-500 + 212)/T$	14.2	N.R.	a		Atkinson, 1986
$8.58 \times 10^{-18} T^2 \exp(-502/T)$	14.1	N.R.	N.R.	N.R.	Demoore, 1985
$4.27 \times 10^{-12} \exp(-1094/T)$	10.9	329 $\pm$ 110	$(5.1 \pm 1.7) \times 10^5$	265	Singh, 1983
$6.86 \times 10^{-18} T^2 \exp(-348/T)$ d	14.6	N.R.	N.R.	N.R.	Jeong & Kaufman, 1982
N.R.	14	83	1×10^6	300	Cupitt, 1980
$4.27 \times 10^{-12} \exp(-1095/T)$	11	559	3.3×10^5	265	Altshuller, 1980
$4.27 \times 10^{-12} \exp(-1098/T)$	11	365	b	b	Derwent & Eggleton, 1978
$2.1 \times 10^{-12} \exp(-770/T)^d$	15.9	N.R.	N.R.	N.R.	Howard and Evenson, 1976
N.R.	14.5^d	27^c	3×10^6	298	Perry et al., 1976
$(4.27 \pm 0.63) \times 10^{-12} \exp(-1094 \pm 81)/T^d$	10.9	142	9×10^5	265	Davis et al., 1976
N.R.	10.4^d	111	1×10^6	298	Cox et al., 1976

a Lifetime was not reported but, the author suggested using [.OH] = 5×10^5 molecules/cm^3 for the Northern Hemisphere.
b Author used model with seasonal and meridional distributions for [.OH] and Temperature.
c Author reported atmospheric half-life , $T_{\frac{1}{2}}$, atmospheric lifetime was calculated as $T_{\frac{1}{2}}/0.693$.
d Authors conducted their own laboratory experiments to determine rate constants.
N.R. Not Reported

Two researchers, Atkinson 1986 and DeMoore 1985, fitted the experimental data of Jeong & Kaufman, Howard & Evenson, Perry et al. and Davis et al. to a temperature dependent expression for the rate constant. Their results are shown in Table IV-2 and are in good agreement. Evaluating Atkinson's equation at the low and high end of the temperature range (265-300K) seen in Table IV-2 gives a rate constant in the range of:

$$9.1 \times 10^{-14} < k < 14.5 \times 10^{-14} \text{ cm}^3/\text{molecules.second}$$

for the reaction of methylene chloride with hydroxyl radical in the troposphere.

The 24-hour average hydroxyl radical concentration in the troposphere has been estimated to range from 3×10^5 to 3×10^6 molecules/cm^3 (Hewitt & Harrison, 1985). Because hydroxyl radicals are only present during daylight, the actual range for daytime concentrations are twice the 24-hour averages given above while nighttime concentrations are essentially zero. Daytime hydroxyl radical concentrations vary depending on many factors including photolytic activity and the concentration of ozone and other pollutants in the troposphere.

Using the rate constants obtained from Atkinson's equation for 265K and 300K and a range of hydroxyl radical concentrations, the estimated tropospheric lifetime for methylene chloride ranges from:

27 days for [.OH] = 3×10^6 molecules/cm^3, T = 300K
426 days for [.OH] = 3×10^5 molecules/cm^3, T = 265K

As previously stated, the concentration of hydroxyl radicals in the troposphere can vary considerably. However, several researchers recommend 24-hour average hydroxyl radical concentrations which are between 0.5×10^6 and approximately 1×10^6 molecules/cm^3 (Prinn, et al., 1987; Winer, 1987; Singh, 1983; Cupitt, 1980; Cox, et al., 1976; Davis, et al., 1976). By using this range of hydroxyl radical concentrations (0.5×10^6 to 1×10^6 molecules/ cm^3) in conjunction with the rate constants determined from Atkinson's equation for 265K and 300K, the resulting atmospheric lifetimes range from 80 to 250 days.

Even for the shortest atmospheric lifetime estimate of 27 days, methylene chloride will become widely dispersed from its emission source. Thus, it is a persistent pollutant, likely to be transported throughout an air basin before it is degraded by chemical reaction.

The initial reaction of methylene chloride with hydroxyl radical is believed to proceed by hydrogen atom abstraction resulting in the

formation of water and dichloromethyl radical (Howard and Evenson, 1976; Davis, et al., 1976; Cox, et al., 1976). Equation 2 summarizes the initial step in the reaction of methylene chloride with hydroxyl radical.

$$CH_2Cl_2 + .OH \text{ -------->} .CHCl_2 + H_2O \quad (2)$$

The subsequent reactions of this radical are as follows (Equation 3) (Atkinson and Winer, 1987). The $CHCl_2$ radical will rapidly react with O_2 to form the peroxy radical.

$$CHCl_2 + O_2 \text{ --------> } OOCHCl_2 \quad (3)$$

This peroxy radical will then react with NO (if present), HO_2 radicals (to form dichloromethylhydroperoxide) or other peroxy (RO_2) radicals (Equations 4 through 6):

$$OOCHCl_2 + NO \text{ --------> } OCHCl_2 + NO_2 \quad (4)$$

$$OOCHCl_2 + HO_2 \text{--------> } HOOCHCl_2 + O_2 \quad (5)$$

$$OOCHCl_2 + RO_2 \text{--------> } OCHCl_2 + \text{other products} \quad (6)$$

These reactions have not been experimentally studied; rather they are expected to occur based on our knowledge of the atmospheric reactions of other simple alkyl peroxy and haloalkyl peroxy radicals. The $CHCl_2O$ radical is known to eliminate a chlorine atom to form formyl chloride (reaction 7) (Niki, et al., 1980):

$$OCHCl_2 \text{---------->} HC(O)Cl + Cl \quad (7)$$

The Cl atom will react with whichever organics are present (in the cleaner troposphere this will be mainly with methane) to yield HCl and lead to the formation of O_3 if NO_x is present.

As previously stated, the most important atmospheric removal mechanism for methylene chloride involves its reaction with hydroxyl radicals. Although other atmospheric removal mechanisms such as photolysis and physical removal play an important role for some compounds that enter the atmosphere, they are expected to be insignificant in the removal of methylene chloride (Winer, 1986).

A 1980 EPA document reports photolysis as a possible process by which methylene chloride can be removed from the atmosphere (U.S. EPA, 1980). Photolysis was listed as possible because chlorinated compounds often absorb in the solar radiation region of the troposphere. However, if photolysis does occur, it is expected to be negligible compared to

removal by the reaction of methylene chloride with hydroxyl radicals (Cupitt, 1986). This is supported by Dilling who attempted to determine the rate of photolysis for methylene chloride in the presence of NO and NO_2. The results demonstrate that methylene chloride is not reactive in the presence of NO or NO_2 when exposed to ultraviolet light at an intensity near that of natural sunlight (Dilling, 1976).

Hydrolysis is not expected to be an important mechanism by which methylene chloride is degraded in the environment. Dilling experimentally determined the hydrolytic half-life to be 18 months in water at 25°C (Dilling et al., 1975). Most methylene chloride entering natural waters is expected to evaporate long before hydrolysis would occur. Under experimental conditions Dilling determined an evaporative half-life of 18 to 25 minutes. Water initially containing approximately 1 ppm methylene chloride was held at 25°C and stirred at 200 rpm. The average solution depth was 6.5 cm (Dilling et al., 1977).

Information concerning physical removal processes for atmospheric methylene chloride is sparse; however, both wet and dry deposition have been reported to be unlikely to occur at a significant rate (U.S. EPA, 1980).

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APPENDIX I

ARB ANALYTICAL METHODS FOR SAMPLING AND ANALYSIS OF ATMOSPHERIC METHYLENE CHLORIDE

October 1986

AIR RESOURCES BOARD
PROCEDURE FOR THE SAMPLING AND ANALYSIS OF ATMOSPHERIC C_1 TO C_2 HALOGENATED HYDROCARBONS

Method 103
Revision 2

Haagen-Smit Laboratory Division
State of California
Air Resources Board
9528 Telstar Avenue
El Monte, CA 91731

Procedure for the Sampling and Analysis of Atmospheric C_1 to C_2 Halogenated Hydrocarbons Method 103

1 Introduction

1.1 This procedure describes a method of sampling and analyzing atmospheric concentrations of C_1 to C_2 halogenated hydrocarbons in the range of 0.004 to 1.0 parts per billion (ppb).

1.2 Lower concentrations may be analyzed by increasing the sample volume and using a cryogenic trap to concentrate the sample.

1.3 Higher concentrations may be analyzed by direct injection of a diluted sample into a sample loop of a gas chromatograph.

1.4 Compounds which can be analyzed by this method are:

1.4.1 Dichloromethane, CH_2Cl_2, (methylene chloride)

1.4.2 Trichloromethane, $CHCl_3$, (chloroform)

1.4.3 1,2-Dichloroethane, $ClCH_2CH_2Cl$, (ethylene dichloride, EDC)

1.4.4 1,1,1-Trichloroethane, Cl_3CCH_3, (methyl chloroform)

1.4.5 Tetrachloromethane, CCl_4, (carbon tetrachloride)

1.4.6 Trichloroethene, $Cl_2C=CHCl$, (trichloroethylene, TCE)

1.4.7 1,2-Dibromoethane, $BrCH_2CH_2Br$, (ethylene dibromide, EDB)

1.4.8 Tetrachloroethene, $Cl_2C=CCl_2$, (perchloroethylene, PERC)

2 Method

2.1 Air is sampled into a Tedlar bag at a calibrated and controlled flow during selected time intervals as described in Appendix A, "Procedure for Atmospheric Tedlar Bag Sampling".

2.2 A measured volume of the air sample is transferred by a syringe into the chromatograph.

2.3 The components are separated by a specified column and analyzed by an electron capture detector.

2.4 An electronic integrator quantitates the halogenated hydrocarbons by integrating the peak areas and calculating concentrations from a factor determined during calibration with a halogenated hydrocarbons

standard mixture.

3 Apparatus

3.1 A sampler with bags is required for each site. The sampler and bags are prepared and operated as described in the "Procedure for Atmospheric Tedlar Bag Sampling".

3.2 A gas chromatograph (GC) equipped with a gas injection valve and freeze-out trap inlet system is required. An electron capture detector is used.

3.3 One GC column is required: A glass column (6 ft x 1/4 in O.D.) packed with 0.2 percent Carbowax 1500 on Supelco 80/100 mesh Carbopac C.

3.4 Other GC supportive apparatus used are a strip chart recorder, a remote controller, and an electronic integrator.

3.5 Ground glass syringes (50, 100, and 250 mL capacity) or other suitable devices to accurately transfer air samples from Tedlar bags to the sample inlet of the GC are used.

3.6 A large air-tight chamber is used to prepare standard gas mixtures.

3.7 The cryogenic traps holding the liquid nitrogen are Dewar containers.

4 Reagents

4.1 All gases used in the GC analysis shall be of the highest commercial quality available.

4.2 Helium shall have a purity of 99.995%.

4.3 Halogenated hydrocarbons reference liquid standards, 99% purity as listed in 1.4 are used to prepare a 10 ppb working standard mixture which is used as a span gas.

4.4 A mixture of 10 percent methane in argon is used as make-up gas in the GC.

4.5 Commercial liquid nitrogen (b.p. = -196°C) is used to cool the freeze-out trap.

5 Procedure

5.1 Bags and samplers are fabricated, tested, and operated as described in Appendix B, "Procedure for the Fabrication and Testing of Sample Bags".

5.2 The air sample is analyzed for C_1 to C_2 halogenated hydrocarbons by using either the loop method or the freeze-out trap method. The freeze-out trap method is used for ppb to ppt (parts per trillion) concentrations.

5.2.1 The procedure for the loop method follows:

5.2.2 The air sample is transferred from the gas sample bag and injected into the sample loop of the GC using a clean 100 mL syringe fitted with a Luer-lok to quick-connect adapter.

5.2.3 The gas sampling valve (rotary type) is equipped with a 1 mL loop.

5.2.4 The gas sampling valve is rotated and the sample enters the GC analyzer and is separated into component compounds.

5.2.5 A Carbowax 1500/Carbopak C column is used to separate the halogenated hydrocarbons. Typical operating conditions for the gas chromatograph are:

25 mL/min helium carrier gas flow
40 mL/min 10% methane in argon make-up flow gas
80°C 10-port valve compartment temperature
150°C injection port temperature
350°C detector temperature
6° to 160°C at 8°C/min programming column temperature
Backflush: 23 min.

5.2.6 Each separated component passes through the electron capture detector and yields a response proportional to its response factor and concentration.

5.2.7 Concentrations of halogenated hydrocarbons may be calculated using an electronic integrator.

5.3.1 The procedure for the freeze-out method follows:

5.3.2 Immerse the sample trap in liquid nitrogen (LN_2) and allow the temperature to stabilize while maintaining a flow of helium through the system.

5.3.3 After discarding about 50 mL of the sample, withdraw exactly 100 mL from the sample bag with a 100 mL syringe and transfer the sample into the trap.

5.3.4 Backfill the syringe with another 40 mL of helium and flush the 40 mL through the trap; then flush the carrier helium through the trap for three minutes.

5.3.5 Isolate the cryogenic trap by using the isolation valve which allows the carrier gas to by-pass the trap.

5.3.6 Replace the LN_2 Dewar flask with a Dewar containing hot water at about 90 deg C.

5.3.7 Allow the trap to warm up.

5.3.8 Inject the sample into the carrier gas stream by turning the GC sampling valve. The gas sample enters the GC analyzer and is separated into component compounds.

5.3.9 The instrument operating conditions are the same as those described in Section 5.2.5 above.

5.3.10 Each separated component passes through the electron capture detector and yields a response proportional to its response factor and concentration.

5.3.11 Figure 5.3.11 is a typical halogenated hydrocarbon chromatogram.

6 Calculations

6.1 The concentrations of halogenated hydrocarbons, in ppb, are calculated by an electronic integrator using the external standard method.

6.1.1 Concentration = Area x Response Factor x Dilution Factor

6.2 The Response Factor (RF) is calculated during calibration by the equation:

$$RF = \frac{\text{Concentration}}{\text{Area}}$$

6.2.1 $$\text{Dilution Factor} = \frac{\text{Total volume of diluted sample}}{\text{Initial sample volume before dilution}}$$

6.2.2 Replicate calibrations are averaged and the arithmetic mean is stored as the RF for subsequent analyses.

6.3 Concentrations may be converted from ppb to mg/m^3 by means of the following formula:

$$mg/m^3 = \frac{P \times (M.W.) \times (ppb) \times (10^6)}{(82.05) \times (T)}$$

Where:

P	=	Pressure in atmospheres
M.W.	=	Molecular weight of corresponding halogenated hydrocarbon
82.05	=	Gas constant in $cm^3 \times atm. / {}^oK\text{-mole}$
T	=	Absolute temperature (^oK).

6.4 The concentration unit mg/m^3 is equivalent to ng/cm^3

6.5 The limit of detection (LOD) for each compound is calculated by means of the following formula:

$$LOD = 3(RSD)\frac{(avg.\ conc.)}{m}$$

Where:

RSD = Relative standard deviation.
avg. conc. = Mean count of the smallest discernable analytical signal.
m = Instrument calibration factor.

7 Quality Control

7.1 Quality control procedures are followed in two areas: sampling and analysis.

7.2 The quality control procedures used in sampling are:

7.2.1 The Tedlar bag samplers are checked every 6 months for leakage and contamination. The interval is shortened if any malfunction is suspected. A written record is maintained of the history of each sampler. (See Appendix A).

7.2.2 The Tedlar bags are checked for leakage and contamination before being used for sampling. A log book is maintained with a complete history of bag usage. (See Appendix B).

7.3 The quality control procedures used in analyzing the sample are:

7.3.1 The accuracy of the method has not been determined.

7.3.1.1 Every six to nine months a calibration standard is prepared in a glass-lined Pfaudler Chamber maintained by the Environmental Laboratory Section of the Haagen-Smit Laboratory.

7.3.1.2 The chamber is repeatedly evacuated and flushed with zero air until it is shown by gas chromatographic analysis to be free of any significant contamination.

7.3.1.3 To prepare the standard, the chamber is re-evacuated and filled with zero air to a pressure of 5 psia.

7.3.1.4 A measured volume of a volumetrically prepared solution of halogenated hydrocarbons in methanol is injected via a heated injector into a stream of zero air as it is flowing into the chamber. The volume of the solution injected into the chamber is chosen so as to give the

desired gas phase concentration of halogenated hydrocarbons when the chamber is pressurized to 16 psia with zero air.

7.3.2 Calibration standards are prepared periodically. The accuracy of the standard is verified and the procedure validated by comparing the concentration of tetrachloroethene in the chamber to that of an NBS standard.

7.3.2.1 A newly prepared chamber working standard is rejected unless the tetrachloroethene concentration based on calculation agrees within +/- 5% of the value determined by analysis, using the NBS standard for calibration.

7.3.2.2 A newly prepared chamber working standard is rejected unless the relative response factors for all eight halogenated hydrocarbons of interest fall within +/- 10% of the historically established mean values.

7.3.3 A working chamber standard is checked at least every three months for conformity to criteria 7.3.2.1 and 7.3.2.2.

7.3.3.1 A new standard is prepared as frequently as required as determined by the above mentioned criteria.

7.3.3.2 Any reports generated after the standard ceases to be demonstratively within the established tolerances shall contain a cautionary explanation.

7.4 The gas chromatograph is calibrated periodically.

7.4.1 Calibration factors are determined on the basis of the mean values of the previous calibration runs which meet the criteria of 7.4.3.

7.4.2 Each day a calibration check is performed using the Pfaudler chamber standard to span the instrument.

7.4.3 If the response for each compound of interest is within 10% of the established calibration value, the established calibration factors are retained.

7.4.4 The calibration check is repeated if the response of the instrument has changed by more than 10% from the established values.

7.4.5 If the response is still out of tolerance, a quality assurance report is submitted, remedial action is initiated, and new calibration factors calculated.

7.4.6 Blank samples shall be analyzed daily after the calibration

is completed and, whenever necessary, between samples.

7.5 The linearity of the instrument is checked periodically.

7.5.1 A gas chromatographic multipoint linearity check is performed annually with standards of at least four different concentrations and four replicate runs for each concentration. The concentrations should include the anticipated range of sample concentrations above the limit of detection.

7.5.2 The mean-square error due to lack of fit about the regression line is compared to the total mean-square error of the independent replicates about their individual means. The calibration is accepted if the F-ratio is less than the 95% rejection limit.

7.5.3 A repeated multipoint calibration should not differ from the previous calibration by more than 10%.

7.5.4 Any region of concentration that deviates more than 5% from the least-square line is considered nonlinear.

7.5.5 Data is reported only for compounds whose concentrations lie in the linear range.

7.6 Limits of detection are established.

7.6.1 The limit of detection (LOD) is based on three standard deviations (SD) of runs near the LOD (within 10 SD of the LOD, Winefordner and Long, 1983).

7.6.2 The LOD should be determined at least on an annual basis.

7.6.3 If the instrument response changes by more than 15%, the instrument must be checked and the LOD redetermined.

7.6.4 The presence in a sample of a very large adjacent peak will often raise the LOD in the sample.

7.7 Analytical instruments have quality control procedures.

7.7.1 Column conditions are checked periodically and as needed.

7.7.1.1 All GC accessible parameters is logged when a column is first installed. These parameters are checked daily and recorded on integrator reports.

7.7.1.2 The efficiency and resolution of the column are checked every month. If the tests show more than a 10% change, the column is replaced.

7.7.1.3 If the headpressure required to maintain a specified

flow through the column increases by more than 100%, the column is replaced.

7.7.1.4 If the drift of retention times of peaks results in peak misidentification, all instrument parameters are checked.

7.7.2 Replicate analyses are a quality control procedure.

7.7.2.1 A duplicate analysis is performed on at least one sample per day.

7.7.2.2 If the duplicate analysis (replicate) differs by more than 20%, and if the concentration of the sample is higher than 3X LOD, then an additional analysis is performed.

7.7.2.3 If the range of the replicate analyses is greater than the mean and if the concentration of the sample is greater than 3X LOD, the analyses are not acceptable.

7.7.2.4 If the range is within 20%, the mean and the standard deviation are reported.

7.7.2.5 If there is any reason to suspect the presence of an interferent (peak broadening, shift of retention time, shoulder formation, etc.), peak identification is verified using another analyzer (GC/MS), detector, or column.

7.7.2.6 When spiked samples are analyzed, the peak height and peak area ratios of the spiked and unspiked samples must be consistent.

7.7.3 Compound confirmation is a quality control procedure.

7.7.3.1 Ten percent of the analyses are confirmed by a different analytical system (different column or different detector, e.g. GC/MS).

7.7.3.2 If the confirmatory and the routine analyses differ by more than 20%, none of the analyses are acceptable.

7.8 Analytical reports undergo quality control procedures.

7.8.1 Data storage: raw data transmitted from the integrator are stored unmodified in electronic storage. Data are archived according to date, site, analyses, and project for easy retrieval. These data are kept for 3 years in the laboratory electronic storage.

7.8.2 All data above the minimum detection limits are reported to the requesting agency in hard copy or electronic format.

7.8.3 All reports are reviewed by at least two qualified staff before they are released.

8 Critique and Comments

8.1 Lower limits of detection have been established using the prescribed instrument conditions and using a 100 mL sample with the freeze-out trap technique.

8.1.1 Table 8.1.1 lists the lower limits of detection for the the compounds analyzed by this method.

8.2 Interferences are not usually a serious problem for light halogenated hydrocarbon analysis when the electron capture detector is used.

8.2.1 The electron capture detector is selective for the measurement of halogenated hydrocarbons. It is virtually insensitive to other hydrocarbons thus eliminating interferences from non-halogenated hydrocarbons.

8.2.2 Any halogenated hydrocarbons present in the sample having retention times very similar to the compounds of interest under the operating conditions described in this method will interfere. Therefore, proof of chemical identity requires confirmation.

8.2.3 Water vapor at normal ambient humidity in the sample does not interfere with the separation and quantification of halogenated hydrocarbons.

8.2.4 High concentrations of nitrogen oxides (500 ppm) and sulfur oxides (50 ppm) interfere in the determination of methylene chloride in the samples of stack emission sources.

8.3 The procedure described herein has both advantages and disadvantages:

8.3.1 This method provides a simple way of air sampling. The concentrations of halogenated hydrocarbons in the range of interest are stable for more than 24 hours in the bag, providing sufficient time for the analysis.

8.3.2 The sample is easily and repeatedly introduced into the instrument by means of a gas sampling valve.

8.3.3 A representative composite sample is readily obtained for any selected time interval because the air sampling flow rate is constant.

8.3.4 Both the upper and the lower limits of detection can

be extended by concentrating a larger volume of the sample with a freeze-out trap or by diluting the sample in a Tedlar bag with nitrogen or by loop injection.

8.3.5 Interferences can be eliminated by selecting chromatographic conditions.

9 References

9.1 U.S. Environmental Protection Agency (19760, "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I-Principles", EPA-600/9-76-005 Environmental Monitoring and Support Laboratory, Research Triangle Park, North Carolina 27711.

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CAUTION Laboratory Operations Involving Carcinogens

Most halogenated hydrocarbons are identified as human carcinogens; therefore, appropriate precautions should be observed when handling these compounds. Do not release halogenated hydrocarbon vapors to the laboratory atmosphere at any time. When venting or purging, the vapor must be routed to outside air. The OSHA regulations pertaining to the use and handling of halogenated hydrocarbons are published in Title 29 of the Code of Federal Regulations available in the Federal Register, Volume 40, May 28, 1975, pp. 23073.

TABLE 8.1.1
LIMITS OF DETECTION

Compound	Limit of Detection ppb	Concentration ppb	Mean Area	Area St.Dev.	n	% Rel St.Dev.
Methylene Chloride	1	1.37	8,230	800	6	9.7
Chloroform	0.004	0.006	8,290	197	5	2.4
Methyl Chloroform	0.004	0.004	34,000	3600	5	10.6
Carbon Tetrachloride	0.02	0.028	13,900	676	5	4.9
		0.01	2,400	320	6	13.3
Trichloroethylene	0.005	0.0064	15,600	515	5	3.3
Ethylene Dibromide	0.01	0.009	3,150	430	5	13.7
Perchloroethylene	0.004	0.0047	102,700	6080	5	5.9
Ethylene Dichloride	0.2	0.3	61,778	4811	6	7.8
		0.09	26,677	2143	5	8

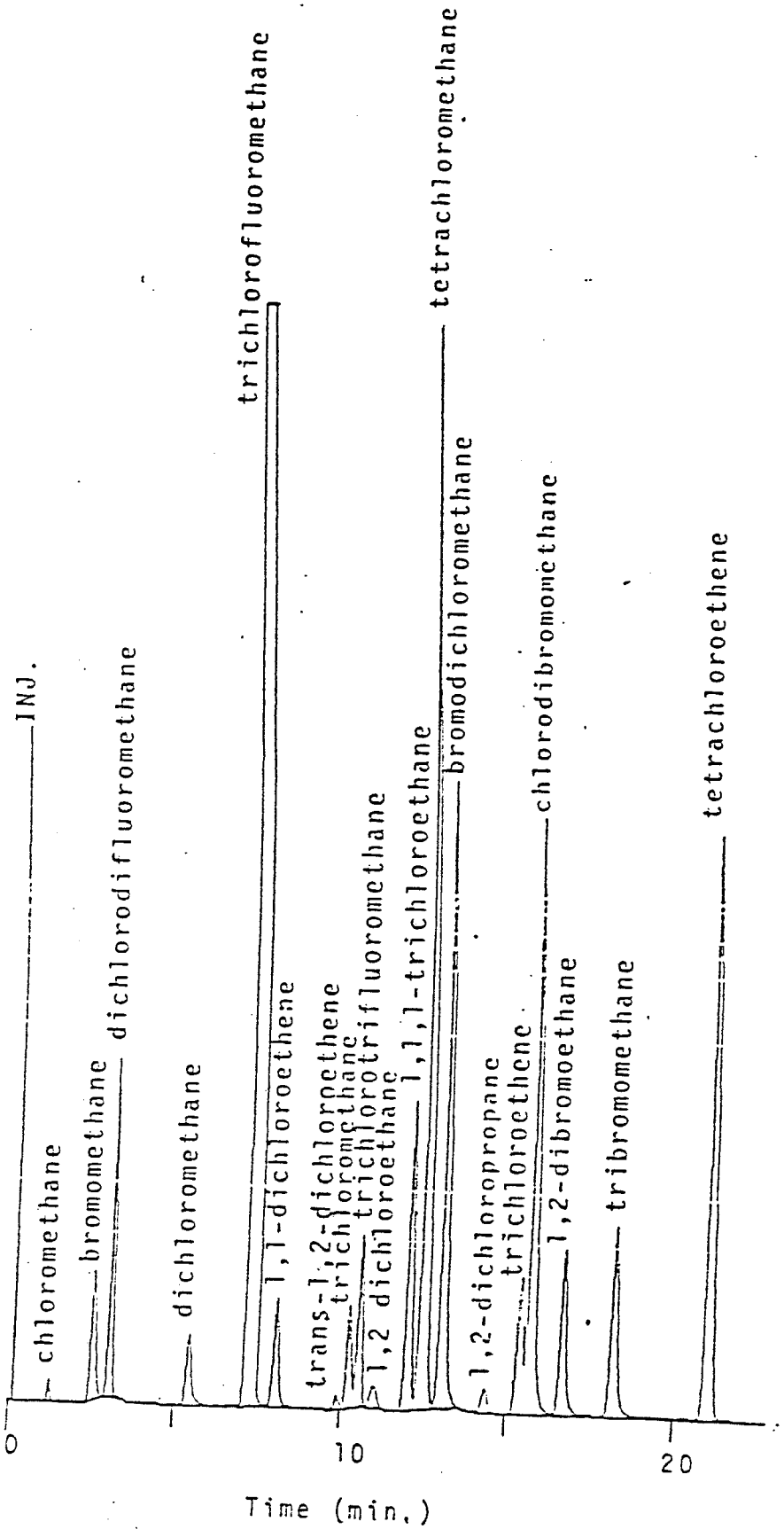


Figure 5.3.11 - Typical Halogenated Hydrocarbon Chromatogram

METHOD NO. ADDL002

STANDARD OPERATING PROCEDURE FOR THE DETERMINATION OF VOLATILE ORGANICS IN AMBIENT AIR USING TENAX TRAP PRECONCENTRATION GAS CHROMATOGRAPHY AND TANDEM PHOTOIONIZATION/ELECTRON CAPTURE DETECTORS

1.0 SCOPE

This document describes a procedure for the determination of volatile halogenated hydrocarbons and aromatics having a boiling point of less than 120°C. This procedure is based on documents received from the ARB Haagen-Smit Laboratory, El Monte, as well as EPA Method TO1.

2.0 SUMMARY OF PROCEDURE

Ambient air is continuously sampled and collected in a Tedlar bag over a 24 hour period and immediately sent to the laboratory for analysis. A sample from the bag is drawn through a sampling valve attached to a Tekmar LSC-2 Tenax Sample Concentrator (see Figure I) with a vacuum pump at 50 cc/min for four minutes (total sample volume: 200 cc). The organic constituents are trapped on Tenax and when the collection is complete, the Tenax is purged with 40 cc of helium to remove any trapped moisture. The sample is then thermally desorbed onto the head of the GC column. The GC column is temperature programmed and component peaks

eluting from the column are sequentially detected and quantified, first by a photoionization detector (PID) and then by an electron capture detector (ECD). The components are identified based on retention times. Positive identification or confirmation requires the use of an appropriately configured GC/MS.

3.0 INTERFERENCES/LIMITATIONS

a. Components having similar GC retention times will interfere, causing misidentification and/or faulty quantitation.

b. Because of the very low sample concentrations, extreme care must be taken to insure that the sample is not degraded or contaminated by the Tedlar sampling bag, sampling apparatus, or delayed delivery to the laboratory. Exposure of the Tedlar sampling bag to temperatures greater than 25°C should be minimized.

c. Only components of the sample which can be detected by PID/ECD detectors will be quantified.

4.0 APPARATUS

a. Varian Model 6000 Gas Chromatograph/PID/ECD system equipped with a Varian Vista 402 dual channel data system.

b. Tekmar LSC-2 Sample Concentrator equipped with Tenax trap and sampling valves as shown in Figure 1.

c. Matheson Model 8240 Mass Flow Controller accurately calibrated in the 5-100 cc/min range.

d. Laboratory timer, accurate to within 0.1 minutes.

e. Gas tight microliter syringe, 50 ul.

f. GC column - 10' x 2 mm i.d. glass column packed with 1 percent SP-1000 on Carbopack B, 60/80 mesh.

5.0 REAGENTS

a. Primary Gas Standard (Scott Specialty Gases - Research Triangle Institute Certified Series 1)

Compound	Concentration (ppb)
Chloroform	107
Carbon tetrachloride	105
Perchloroethene	106
Vinyl chloride	104
Benzene	107

b. Primary Gas Standard (Scott Specialty Gases - Research Triangle Institute Certified Series 2)

Compound	Concentration (ppb)
1,2-Dichloroethane	101
1,1,1-Trichloroethane	98
Trichloroethene	100
1,2-Dibromoethane	102

c. Stock Gas Standard - Scott-Marrin Blend (assayed against primary cylinders)

Compound	Concentration (ppb)
Dichloromethane	4272
Chloroform	528
1,2-Dichloroethane	3104
1,1,1-Trichloroethane	424
Carbon tetrachloride	46
Trichloroethene	336
1,2-Dibromoethane	5
Perchloroethene	43
Vinyl chloride	4736
Benzene	1888

d. Control Gas Standard - Scott-Marrin blend (assayed against primary cylinder)

Compound	Concentration (ppb)
Dichloromethane	6
Chloroform	0.2
1,2-Dichloroethane	0.2
1,1,1-Trichloroethane	3.6
Carbon tetrachloride	0.3
Trichloroethene	1.8
1,2-Dibromoethane	2.5
Perchloroethene	1.2
Vinyl chloride	3.3
Benzene	4.8

e. Surrogate Gas Standard (Scott-Marrin Blend)

Compound	Concentration (ppm)
Bromochloromethane	10
1,3-Bromochloropropane	33

6.0 PROCEDURES

a. Sample Trapping

1. The preconcentration system is shown in Figure 1.

2. The high concentration inlet is used for high concentration calibration standards and for other samples with concentrations higher than ambient levels. The sample is introduced through the high concentration inlet and 6 port valve into an appropriate size loop of known volume. The sample then passes through a 10 port valve, mass flow meter, and vacuum pump. Before an analysis, the system is leak checked by blocking the sample inlet port and observing that the mass flow meter reading drops to zero. The high concentration inlet then is connected to a Tedlar sample bag valve and the gas bag valve is opened. The loop is then flushed with sample gas for three minutes. After three minutes of flushing, the 6 port valve is reset so that the sample contained in the loop is carried into the trap by the helium purge gas. This continues for three minutes to ensure that all of the contents of the loop are trapped.

3. Ambient samples are introduced from Tedlar bags as described above, except that the sample loop is bypassed and the sample goes directly to the 10 port valve. After flushing the system with sample for three minutes, the 10 port valve is reset so that 200 cc's of sample is trapped (50 cc/min. for four minutes). After sample trapping is complete, the Tenax trap is flushed with 40 cc of helium to remove water vapor and any nonadsorbed reactive gases.

4. In both ambient and high concentration cases, after the sample has been trapped, the Tekmar LSC-2 heats the Tenax trap to 180°C while the trap is swept with the G.C.'s internal carrier gas for four minutes. The contents of the trap are thus desorbed and collected on the head of the G.C. column. The trap is baked out after the end of the desorption cycle. In the bakeout cycle, the trap is flushed with helium purge gas for eight minutes while being held at 225°C in order to prepare the trap for the next cycle. After bakeout the trap is isolated from the system and ready for the next sample.

b. Analysis

1. The concentrated sample is separated under the chromatographic condition detailed below. The resulting chromatogram (see Figure II) is then integrated and quantified by reference to calibration standard gases.

2. Instrument Conditions:

GC: Column: 10' x 2 mm i.d. glass column, packed with 1 percent SP-1000 on Carbopack B 60/80 mesh

Temperatures: Injection: 200°C
Detector: 350°C
Oven: 45°C, hold for four minutes, 5°C/min ramp, to 210°C, hold for eight minutes

Flow Rates: Carrier: He, 20 cc/min
ECD make up: N_2, 40 cc/min

Detectors: ECD: Range X 10, Attenuation X 32
PID: Range X 1, Attenuation X 32, 10.2 ev lamp

Conc: Tekmar LSC-2: Purge: 4 minutes
Desorb: 4 minutes at 180°C
Bake: 8 minutes at 225°C

3. All blanks, standards, control samples, and ambient samples are spiked with surrogate compounds by injecting 50 microliters of the surrogate gas standard (5.e.) during sample trapping. The surrogate compounds, chosen such that they simulate the characteristics of the analytes of interest and are unlikely to occur in the environment, are added to insure that systematic errors or equipment failures will be noted and corrected promptly.

4. The first step in a calibration is to analyze a system blank. This is done by trapping and analyzing a 200 cc sample of auxiliary carrier gas. The system blank must be free of interfering peaks. A system blank must also be run after a high concentration sample is analyzed in order to detect any carry-over within the system.

5. A calibration is performed using a 1.25 cc loop of stock standard gas (5.c.). Two hundred cubic centimeters of helium gas is passed through the loop to carry the standard onto the trap. The calibration analysis is made as a normal analysis. The calculated concentration value for each component should be inspected to insure consistency with previous analyses. The stored chromatographic information may then be used to recalculate the response factors for the subsequent analyses. The G.C. data system will not accept updated response factors which are in excess of plus or minus 15 percent of historic data.

6. Following calibration, 200 cc of the control sample (5.d.) is concentrated on the trap and analyzed. The control sample data are plotted on control charts of the normal Shewhart type. Upper and lower warning limits are plus or minus two times the standard deviation. Any analysis which falls outside the upper and lower warning limits is repeated and the laboratory quality control officer is advised. Upper and lower control limits are plus or minus three times the standard deviation. If any analysis falls outside the upper or lower control limit, the method is discontinued until the out of control situation is remedied. The laboratory quality control officer is advised and provided with written documentation of the out of control condition and how it was remedied. All data generated prior to the out of control situation must be reviewed for possible decertification by laboratory management.

7. Multipoint calibrations are conducted monthly. Each multipoint calibration includes a trap blank and three standard concentration levels to bracket the concentration ranges expected in ambient air. If subsequent data indicate that the resulting least squares analyses are consistently acceptable, less frequent multipoint calibrations may be made.

7.0 PERFORMANCE

a. All ambient field samples are analyzed in duplicate. The relative error between analyses must be less than 20 percent. Duplicate analyses having greater than 20 percent relative error must be decertified.

b. The percent recovery of the surrogate is recorded in the instrument laboratory workbook for each analysis. If this value is outside the 80% to 120% range, the sample analysis must be repeated.

8.0 METHOD SENSITIVITY, PRECISION AND ACCURACY

The method sensitivity, precision and accuracy are outlined in Table I. These data were produced with gaseous calibration standards, and using carrier gas as the sample matrix. The relative accuracy of the method, with the exception of dichloromethane, is based on reference to the Research Triangle Institute Certified Gas Standards (NBS traceable). Authoritative reference calibration standards for dichloromethane are under development at NBS but are not yet available. The concentration value of the present standard was assigned by the commercial manufacturer and found to be in good agreement with diluted pure dichloromethane prepared in our laboratory. The absolute accuracy of the method has not been determined by interlaboratory testing.

Figure I

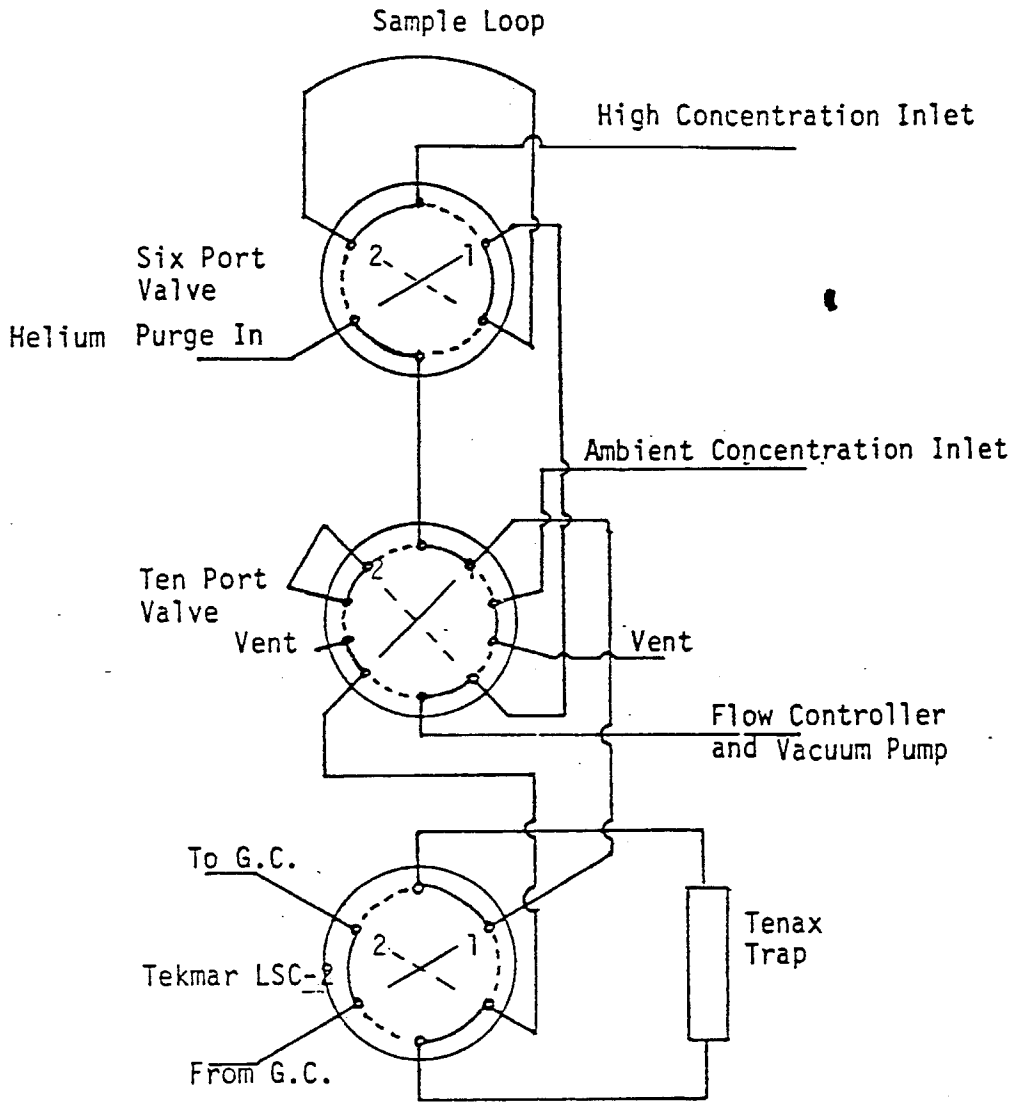


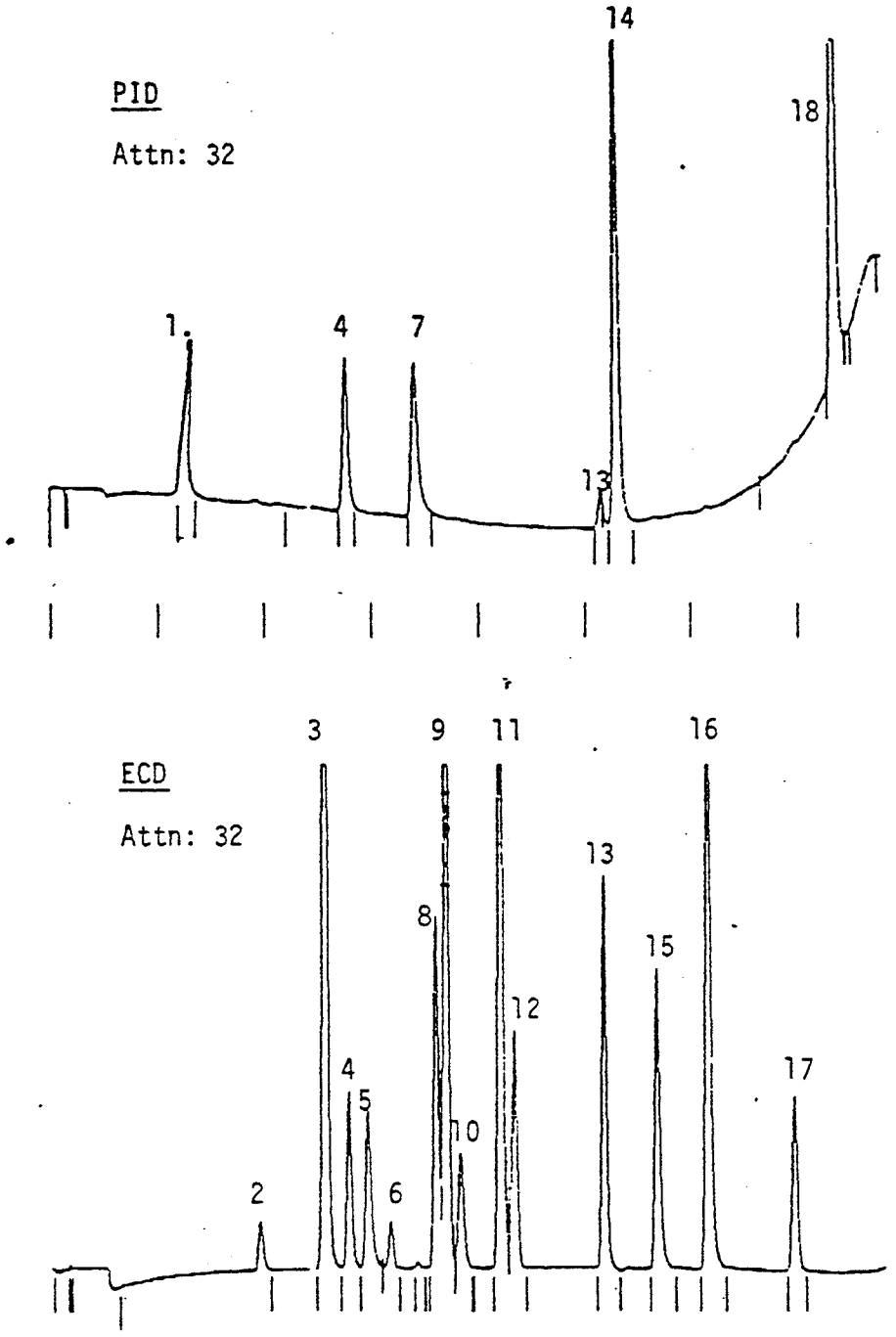
Figure 1. Schematic of concentrator system. Sampling Conditions are: 200 cc volume, purge at 40cc/min, 1 min., desorb at 180 C for 4 min., bake for 8 min. at 225 C.

SYSTEM GUIDE

Operational Step	Valve Position			
	6-Port	10-Port	LSC-2	Purge Gas
Loop Fill	1	1	1	Off
Loop Trap	2	1	1	On
Ambient Trap	1	2	1	Off
Trap Desorb	1	1	2	Off
Trap Bake Out	1	1	1	On

Figure II

Standard PID/ECD Organic Analysis



1. Vinyl Chloride
2. Dichloromethane
3. Trichlorofluoromethane
4. 1,1-Dichloroethylene
5. Bromochloromethane
6. 1,1-Dichloroethane
7. t-1,2-Dichloroethylene
8. Chloroform
9. Freon 113
10. 1,2-Dichloroethane
11. 1,1,1-Trichloroethane
12. Carbon Tetrachloride
13. Trichloroethylene
14. Benzene
15. 1,2-Dibromoethane
16. Bromochloropropane
17. Tetrachloroethylene
18. Toluene

Table I

Method Sensitivity and Precision

Compound	Correlation Coefficient	Slope	R.S.D* (Percent)	Detector	LOD ppbv
Vinyl Chloride	0.997	0.946	16	PID	0.8
Dichloromethane	0.999	0.975	5	ECD	0.6
1,1-Dichloroethylene	0.991	0.966	6	ECD	0.05
Chloroform	0.999	0.901	3	ECD	0.02
1,2-Dichloroethane	0.999	1.054	7	ECD	0.1
1,1,1-Trichloroethane	0.999	0.989	9	ECD	0.01
Carbon Tetrachloride	0.999	0.980	6	ECD	0.005
Trichloroethylene	0.999	0.992	6	ECD	0.02
Benzene	0.998	0.950	10	PID	0.5
1,2-Dibromoethane	0.974	1.067	9	ECD	0.005
Tetrachloroethylene	0.994	1.080	10	ECD	0.01

* R.S.D. - Relative Standard Deviation at 5 x LOD, n = 5

APPENDIX II

DESCRIPTION OF GLEIT'S METHOD

APPENDIX II

DESCRIPTION OF GLEIT'S METHOD

Gleit's method accounts for the concentrations below the LOD by setting them equal to the "below -LOD mean" μ_{BLOD}, the mean of the portion of the normal distribution below the LOD. Setting the unknown concentrations to their average value seems intuitively reasonable, and the simulations reported in Gleit's paper show that his method is more accurate than other commonly used approximations.

The below-LOD mean of a normal distribution of a variable with a limit of detection L is given, in terms of L and the mean μ and the standard deviation σ of the distribution, by equation 1:

$$\mu_{BLOD} = \mu - \sigma * [\, f((L-\mu)/\sigma) / F((L-\mu)/\sigma) \,] \qquad (1)$$

In equation (1), f and F are, respectively, the probability density function and cumulative distribution function of the standard normal distribution. The "Estimated Concentrations for Samples Below the LOD" reported in Table II-2 are the below-LOD means of the assumed lognormal distributions of the concentrations. These below-LOD means are computed from equation (2) in terms of parameters of the associated normal distribution: the LOD L, the mean concentration from Table II-2, and the estimated standard deviation (which is not tabulated).

$$\exp(\mu+0.5^{*}\sigma^{2})^{*} F((L-\mu-\sigma^{2})/\sigma) / F(L-\mu/\sigma) \qquad (2)$$

We now describe how Gleit's method estimates the mean and variance of the assumed normal distribution. The mean and variance cannot be estimated by merely substituting into standard formulas, if below-LOD concentrations are to be set to the below-LOD mean. On the one hand, the mean and variance must be known in order to calculate the below-LOD mean from (1); on the other hand,

the below-LOD mean must be known if it is to be used in the calculation of the mean and variance. Statistical theory, by asserting that a "best -fitting " mean and variance for the distribution exist, provides a way out of this dilemma. Gleit uses a simple iterative procedure to compute these best-fitting parameters. Since his procedure can be simply described in words, a written description is given, supplemented where necessary by equations written in a notation more convenient than Gleit's.

Starting with initial guesses $\mu(0)$ and $\sigma^2(0)$ for the mean and variance, the procedure repeatedly generates new estimates of the mean and variance by the two-step computation described below until successive estimates of the mean and variance converge sufficiently (The K-th pair of estimates are denoted by $\mu(K)$ and $\sigma^2(K)$.). The two steps are:

(a) The K+1-st below-LOD mean $\mu_{BLOD}(K+1)$ is computed by substituting $\mu(K)$ and $\sigma(K)$ (the square root of $\sigma^2(K)$) into equation (1).

(b) The K+1-st estimate of the mean, $\mu(K+1)$, is computed in the usual way with $\mu_{BLOD}(K+1)$ substituted for the sample values below the LOD. The K+1-st estimate of the variance, $\sigma^2(K+1)$, is also computed in the usual way, with an analogous substitution for sample values below the LOD: the squared deviations from the mean of concentrations below the LOD are set equal to the average squared deviation from the mean of the below-LOD portion of the distribution.

Let the N sample items be X(1),....,X(N), and let p be the number of sample items below the LOD. $\mu(K+1)$ is computed by:

$$\mu(K+1) = (1/N)\,\Sigma\, Y(J), \text{ where } Y(J) = X(J) \text{ if } X(J) \geq L$$
$$\text{and } Y(J) = \mu_{BLOD}(K+1) \text{ otherwise.}$$

$\sigma^2(K+1)$ is computed by:

$$\sigma^2(K+1) = (1/N)\,\Sigma\, D^2(J), \quad \text{where } D^2(J) = (X(J) - \mu(K+1))^2$$
$$\text{if } X(J) \geq L, \text{ and } D^2(J) = \sigma^2_{BLOD}(K+1) \text{ otherwise.}$$

The quantity $\sigma^2_{BLOD}(K+1)$, the average squared deviation of the below-LOD portion of the distribution, is computed from the following equation:

$$\sigma^2_{BLOD}(K+1) = \sigma^2(K)^*[1 - Z(K)^* (f(Z(K)) / F(Z(K)))],$$
$$\text{where } Z(K) = ((L-\mu (K)) / \sigma(K)).$$

Gleit's method nearly always converges in a few steps unless there are only a few distinct values above the detection limit, in which case it may converge very slowly. Gleit's method and closely related methods appear to be the best available estimators of the mean when the sample includes values below the LOD, as is demonstrated by the simulations reported in Gleit's paper.

APPENDIX III

METHODS FOR ESTIMATING CALIFORNIA METHYLENE CHLORIDE USE

APPENDIX TO CHAPTER III

Methods For Estimating California Methylene Chloride Usage

Methylene chloride data, collected by source category, was used as the basis for estimating emissions and for comparing the relative consumption of different categories. Thirteen major source categories of methylene chloride use in the U.S. were identified. Estimates of California consumption of methylene chloride were developed for these categories.

Different methods were used to estimate California use for the 13 categories. For several categories, California use was estimated from estimated U.S. use compiled by the Halogenated Solvents Industry Alliance (HSIA, 1985). For other categories, information providing a more direct estimate of California use was available.

Paint removers, aerosols, and miscellaneous:

Population fractions were used to estimate California use from U.S. use for these four categories. California's population was 11 percent of the U.S population in 1980 (U.S. Dept. of Commerce). Thus, California use was estimated as 11 percent of U.S use for these categories.

Pharmaceuticals, Photoresist Stripping, Specialty Chemicals, Chemical Processing & Food Processing:

Domestic manufacturers reported the amounts of methylene chloride that they shipped to California for eleven different end use categories during 1985 (HSIA, 1986b). These figures were reported in Table III-1 as an estimate of California use for the five categories above. They are considered as lower-end estimates because fractions of the 5,400 tons that manufacturers report shipping to California for unidentified miscellaneous use could have been consumed by these five end uses.

Degreasing Operations

Methylene chloride use for degreasing operations in California was determined as the ratio of California employment in applicable SIC categories to U.S. employment in those categories, multiplied by the U.S. use. Five major industry groups used methylene chloride in degreasing operations, including: furniture and fixtures (SIC 25), fabricated metal products (SIC 34), electric and electronic equipment (SIC 36), transportation equipment (SIC 37), and miscellaneous manufacturing industries (SIC 39). Employment data by two-digit SIC

code is available from the Bureau of Census. An EPA report discussed this approach and listed the California use of methylene chloride by degreasing operations as 3,100 TPY in 1983 (U.S. EPA, 1985).

Distribution Facilities:

The quantity of methylene chloride handled by distribution facilities in California was estimated as a ratio of California use to U.S. use times the quantity of methylene chloride handled by U.S. distribution facilities. Use in this case was considered to be the total usage determined for all direct users, as presented in Table III-1 of the text. An EPA report estimated the quantity of methylene chloride handled by U.S. distribution facilities to be 240,000 TPY (U.S. EPA, 1985).

Urethane Foam Manufacturing:

California consumption for foam manufacture is based on estimates made by an EPA contractor. (Pandullo and Nash, 1986). The contractor identified eight California facilities which use methylene chloride. At this time ARB has not verified whether or not these are the only facilities which use methylene chloride for manufacturing urethane foam products in California. Total use by all eight facilities was reported as 1,600 tons in 1984. The manufacturers supplied methylene chloride use for four of the eight facilities. The contractor assumed that for the remaining facilities use was equivalent to the average use (194 tons) of all 43 foam manufacturing facilities in the United States for which methylene chloride consumption was obtained.

Pesticide Manufacturing:

Pesticide manufacturing use is based on information for the one facility in the state that the EPA identified as a user of methylene chloride. Use at this facility was 800 tons in 1983 (U.S. EPA, 1985). It is possible that other pesticide manufacturing facilities located in California are using methylene chloride.

Solvent Reclaimers:

The quantity of methylene chloride sent to solvent reclaimers in California was based on two sources of information: 1) the California Department of Health Services and 2) private industry. The California Department of Health Services collects data from transportation manifests on the quantities of hazardous waste shipped in California. According to these data, 9,685 tons of halogenated solvents were sent to solvent reclaimers in 1985 (DHS, 1986). Representatives of two of the

largest solvent reclaimers in California estimated the percent of methylene chloride in the halogenated solvents received (O'Morrow, 1986; Schneider, 1986). From this information, it was estimated that one fourth or 2,400 tons of the halogenated solvents were methylene chloride in 1985.

Chemical Processing & Specialty Chemical Production:

The HSIA reported that in 1985 1,200 tons of methylene chloride were shipped to California for the chemical processing industry and that 800 tons were shipped into the state for specialty chemical production. Only two facilities in California which fall into these end use categories have been identified. Methylene chloride consumption for both facilities is unknown. It is possible that other chemical processing and production facilities in California use and emit methylene chloride.

The two facilities that have been identified are both in the San Francisco Bay Area Air Basin. One uses methylene chloride in the production of an unidentified specialty chemical and the other uses it to manufacture rubber cement. Both facilities reported emissions data to EPA. Methylene chloride emission estimates are 3 tons per year at the rubber cement production facility (Howie, 1986), and 54 tons per year at the specialty chemical production facility (U.S. EPA, 1985).

Triacetate Fiber Production

Methylene chloride is used as a solvent for triacetate fiber production at one facility in Rockhill, South Carolina (U.S. EPA, 1985). Methylene chloride is not used in this manner in California.

REFERENCES

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Howle, R., 1986. Telephone conversation between Ronald A. Rothacker of CARB and Reese Howle of Radian Corporation, Research Triangle Park, NC. July 22, 1986.

HSIA, 1985. Letters from D.L. Morgan of Cleary, Gottlieb, Steen and Hamilton to R.E. Rosensteel, U.S. IPA, OAQPS, Emission Standards and Engineering Division. Regarding methylene chloride end use data from HSIA member companies. Dated March 8, April 11 and June 28, 1985.

HSIA, 1986a. Letter from D.L. Morgan of Cleary, Gottlieb, Steen and Hamilton to J.A. Marconi of CARB regarding amount of methylene chloride shipped to California. October 28, 1986.

HSIA, 1986b. Letter from D.L. Morgan of Cleary, Gottlieb, Steen and Hamilton to Donald J. Ames of CARB regarding end use of methylene chloride shipped to California by domestic manufacturers. December 23, 1986.

O'Morrow, K., 1986. Telephone conversation between Ronald A. Rothacker of CARB and Ken O'Morrow of Oil and Solvent Process Co., Azusa, Ca., June 9, 1986.

Pandullo, R. and Nash, R., 1986. Radian Corporation memorandum to file entitled: "Estimates of Methylene Chloride Emissions from Polyurethane Foam Slabstock Facilities and Emission Reductions Achievable with Additional Controls," April 28, 1986.

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U.S. Department of Commerce, Bureau of the Census, 1982. Statistical Abstract of the United States 1982-83. 103rd. Edition., December, 1982.

U.S. EPA, 1985. "Survey of Methylene Chloride Emission Sources," EPA-450/3-85-015, Research Triangle Park, NC.

APPENDIX IV

INFORMATION REQUEST LETTER WITH ATTACHMENTS AND RESPONSES

STATE OF CALIFORNIA
GEORGE DEUKMEJIAN, Governor

AIR RESOURCES BOARD
1102 Q STREET
P.O. BOX 2815
SACRAMENTO, CA 95812

Dear Sir or Madam:

Request for Information Regarding
Methylene Chloride (dichloromethane)

I am writing to request information on the health effects of methylene chloride (dichloromethane) as part of our toxic air contaminant program. This program is based on Health and Safety Code Sections 39650, et seq. which require the Air Resources Board (ARB) to prepare a report which would serve as the basis for regulatory action and to determine by regulation, whether a substance is a toxic air contaminant. Once identified as a toxic air contaminant, the law further requires that the ARB prepare a report on the need and appropriate degree of regulation for the substance. After consultation with the staff of the Department of Health Services (DHS), we have selected methylene chloride as a candidate toxic air contaminant to be evaluated in accordance with the provisions of Health and Safety Code Sections 39650, et seq. During our evaluation of methylene chloride, we will consider all available health information regarding this substance. Additionally, we are soliciting information regarding possible biological transformations of methylene chloride.

Before the ARB can formally identify a substance as a toxic air contaminant, several steps must be taken. First, the ARB must request the Department of Health Services to evaluate the health effects of the candidate substance. Second, the ARB staff must prepare a report which includes the health effects evaluation and then submit the report to a Scientific Review Panel for its review. The report submitted to the Panel will be made available to the public. Information submitted in response to this request will be considered in the report to the Panel. Although any person may also submit information directly to the Panel for its consideration, I urge you to submit all information at this time for our consideration in the development of the report for the Panel. The Panel reviews the sufficiency of the

information, methods, and data used by the DHS in its evaluation. Last, after review by the Scientific Review Panel, the report with the written findings of the Panel will be considered by the Air Resources Board and will be the basis for any regulatory action by the Board officially to identify a substance as a toxic air contaminant.

Prior to formally requesting the DHS to prepare a health effects evaluation of methylene chloride, we are providing, pursuant to the provisions of Section 39660(e) of the Health and Safety Code, an opportunity for interested parties to submit information on the health effects of methylene chloride which he or she believes would be important in DHS' evaluation of methylene chloride as a candidate toxic air contaminant.

In January 1986, we conducted a reference search on methylene chloride health effects using the MEDLINE and TOXLINE data bases available from the National Library of Medicine. These information services include material published from 1965 to late-1985. The attached bibliography lists the references from this information search. We are requesting pertinent information on methylene chloride health effects, including any material that may not be available to the public and/or that is not included in the attached bibliography.

Pursuant to the provisions of the Public Records Act (Government Code Sections 6280 et seq.), the information you provide will be public record and subject to public disclosure, except for trade secrets which are not emission data or other information which is exempt from disclosure or the disclosure of which is prohibited by law. The information may also be released to the Environmental Protection Agency, which protects trade secrets and confidential information in accordance with federal law, and to other public agencies, which are also required to protect such information.

To expedite the review process, we ask that any information which you believe should be regarded as "trade secret" be clearly marked and separated from other information. You may identify portions of the information you submit as "trade secret" in accordance with Health and Safety Code Section 39660(e). The claim of trade secrecy must be supported upon the request of the Air Resources Board. Other information claimed to be trade secret and information otherwise claimed to be exempt from disclosure may be identified as confidential in accordance with Section 91011, Title 17, California Administrative Code. Section 91011 requires that the claim of confidentiality be

accompanied by specified supporting information.

I would appreciate receiving any relevant information you wish to submit by March 17, 1986. Your help in expediting our review will be greatly appreciated. Please send the information in duplicate to the attention of:

William V. Loscutoff, Chief
Toxic Pollutants Branch
Re: Methylene Chloride
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

If you have any further questions regarding health effects information, please contact Mr. John Batchelder at (916) 323-1505. For any other questions, please contact Mr. Don Ames at (916) 322-8285.

If you are not the person to whom this request should be addressed, please forward it to the appropriate person in your organization. Also, please let us know whether you would like to continue to receive information inquiries for other candidate substances, and if not, if there is anyone in your organization to whom such requests should be sent.

Sincerely,

Peter D. Venturini, Chief
Stationary Source Division

Attachment

cc: Alex Kelter, DHS
Lori Johnston, DFA
Wayne Morgan, President, CAPCOA
Jan Bush, Executive Secretary, CAPCOA
David Howekamp, EPA Region IX
Assemblywoman Sally Tanner, Chairwoman, Committee on Toxic Materials
Senator Ralph Dills, Chairman, Committee on Governmental Organization
Senator Art Torres, Chairman, Committee on Toxics and Public Safety Management
Emil Mrak, Chairman, and Scientific Review Panel Members
APCOs

HSIA HALOGENATED SOLVENTS INDUSTRY ALLIANCE

2315 M Street, N.W., Third Floor, Washington, D.C. 20037 • (202) 223-5890

March 27, 1986

Mr. William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Branch
P.O. Box 2815
Sacramento, CA 95812

Re: Methylene Chloride

Dear Mr. Loscutoff:

We thank you for providing us the opportunity to submit health information on methylene chloride. We are enclosing a variety of recent documents and articles which were not included in your list of references. Please note that the last two references listed are not enclosed. They are currently being cleared for outside release and should be sent within two weeks.

HSIA understands that this information will be used by the State Department of Health Services in its process of considering all available scientific data in its evalration of health effects and recommendation as to whether or not methylene chloride should be determined to be a toxic air contaminant.

A toxic air contaminant is defined in AB 1807 as:

> An air pollutant which may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health.

HSIA believes that methylene chloride does not cause adverse health effects when used according to current industrial hygiene guidelines or labeled instructions. Furthermore, there is no scientific evidence to indicate that ambient concentrations of methylene chloride cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health. HSIA believes that adequate scientific evidence exists to determine that methylene chloride does not meet the above definition of a toxic air contaminant and should not be identified as one.

We submit the following scientific information as the basis for our conclusion that methylene chloride should not be identified as a toxic air contaminant.

1. Two well-conducted epidemiologic studies have been completed on worker populations exposed to methylene chloride. Neither study indicated a human cancer risk associated with methylene chloride exposure. The most definitive study compare the mortality rate of over 1,000 employees with identified methylene chloride exposure to an unexposed worker population. The findings of this study indicate that workers to methylene chloride for a minimum of 20 years and observed over 20 additional years actually had a decreased incidence of cancer when compared to the New York State control population.

   The other epidemiologic study of methylene chloride examined the health and mortality of over 1200 employees exposed to a mixture of methylene chloride, ethanol, and acetone in a fiber production plant. The study showed no excess mortality cancer in the workers exposed to methylene chloride, even though exposures had ranged up to 475 parts per million and over 300 of them had been followed at least 17-1/2 years after exposure. This study is highly relevant to an understanding of the health risk posed by methylene chloride.

2. The only sites in which methylene chloride has produced tumors are those sites in experimental rodents where the tumors occur spontaneously in unexposed animals (mouse lung and liver tumors and benign mammary gland tumors in rats with no progression to malignancy). The only exception is a low but statistically significant incidence of ventral neck region tumors in male rats only in one study. This response was reviewed and its relevance severely questioned by the U.S. EPA Science Advisory Board and at the Nutrition Foundation Food Solvents Workshop on Methylene Chloride in 1984. Most importantly and of extreme toxicological significance is the fact that the ventral neck region tumor response was not repeatable in the NTP bioassay in rats in any other species evaluated (mouse and hamster).

3. Methylene chloride has been evaluated in numerous short-term in vitro tests, from microorganisms to mammalian cells in culture, as well as in whole animal assays to determine its genotoxic potential. Aside from positive activity in certain microorganisms (primarily bacteria), results in mammalian cells and whole animals, have, for the most part, been negative. A genotoxic component, if present at all in exposed animals is likely to be very weak to nil and not a significant factor in the toxicity of methylene chloride. Thus the principle of practical no-effect-levels should apply in assessing risk for humans.

4. Mechanistic studies have been conducted which provide plausible hypotheses for the observed enhancement of spontaneous tumors in animals exposed to high concentrations of methylene chloride (mouse lung/liver; cytotoxicity/physiological stimulation: rat benign mammary gland; elevated prolactin levels). HSIA believes that humans are not exposed to levels of methylene chloride in the ambient environment which could cause is chain of events to occur. Furthermore, development of a physiologically-based pharmacokinetic model for methylene chloride has confirmed that markedly lower tissue levels of bioactive metabolites of methylene chloride (lower internal dose) would be found in humans than in experimental animals exposed to comparable external concentrations of methylene chloride.

To summarize, HSIA believes that methylene chloride should not be identified as a toxic air contaminant. We have enclosed additional pertinent references to support this belief. In addition we offer our cooperation in answering any questions which might arise in this review of methylene chloride.

Please feel free to call me at (202) 223-5890.

Sincerely yours,

Paul A. Cammer

Paul Cammer, Ph.D.
Executive Director

Enclosure

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** Breslein, W. J. and Landry, T. D. (1986). Methylene chloride: effects on estrous cycling and serum prolactin in Sprague-Dawley rats. Report of the Dow Chemical Co., Midland, MI 48640.

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** Not enclosed. Currently being cleared for outside release.

HALOGENATED SOLVENTS INDUSTRY ALLIANCE
2315 M Street, N.W., Third Floor, Washington, D.C. 20037 • (202) 223-5890

March 31, 1986

Mr. William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Branch
P.O. Box 2815
Sacramento, CA 95812

Dear Mr. Loscutoff:

Our submission of March 27, 1986, contained a typographical error. On page 3, line 8 the word is should be changed to this.

Sincerely,

Thomas Cortina
Assistant Director

HSIA HALOGENATED SOLVENTS INDUSTRY ALLIANCE
2315 M Street, N.W., Third Floor, Washington, D.C. 20037 • (202) 223-5890

April 10, 1986

Mr. William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Re: Methylene Chloride

Dear Mr. Loscutoff:

In my letter of March 27, 1986, I noted that the last two documents listed in our submission would be sent at a later date. Those documents have now been cleared for outside release and are enclosed.

We appreciate your allowing us to submit these documents on a delayed basis and offer our cooperation in answering any questions which might arise in your review of methylene chloride.

Please feel free to call me at (202) 223-5890.

Sincerely,

Paul A. Cammer

Paul A. Cammer, Ph.D.
Executive Director

Enclosures

HSIA HALOGENATED SOLVENTS INDUSTRY ALLIANCE

2315 M Street, N.W., Third Floor, Washington, D.C. 20037 • (202) 223-5890

July 8, 1986

Mr. William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Re: Methylene Chloride

Dear Mr. Loscutoff:

Dr. Alan Schumann, chairman of HSIA's Health and Science Committee, presented a seminar on methylene chloride at DOHS' Berkeley offices on June 4. Enclosed are two copies of the June 24 summary letter which Dr. Schumann sent to Dr. Neutra.

Also enclosed are two copies of the final report for a two-generation inhalation reproduction study in Fisher 344 rats, and the most recent update from CEFIC of their ongoing research program on the species differences in the metabolism of methylene chloride. The reports from the first phase of the CEFIC research program were submitted in March by CEFIC, and they have asked that HSIA submit this latest update.

We would like you to consider the enclosed materials as part of the health information used by the Department of Health Services in its recommendation as to whether or not methylene chloride should be determined to be a toxic air contaminant.

Please feel free to call me at (202) 223-5890 if you have any questions or need further information.

Sincerely yours,

Paul A. Cammer

Paul A. Cammer, Ph.D.
Executive Director

Enclosures

cc: Dr. Raymond Neutra

METHYLENE CHLORIDE PRODUCERS ASSOCIATION

A CEFIC Sector Group

Conseil Européen des
Fédérations de l'Industrie Chimique

European Council of Chemical
Manufacturer's Federations

Your Ref.

Our Ref. SG METHYLENE CHLORIDE

REPLIES TO: Dr M R Harris
Regulatory Affairs
Imperial Chemical Industries PLC
Mond Division, PO Box 13
The Heath, Runcorn, WA7 4QF
CHESHIRE, England

William V Loscutoff
Chief of Toxic Pollutants Branch
Re: Methylene Chloride
California Air Resources Board
PO Box 2815
Sacramento
California 95812
USA

Your ref	Our ref	Date
	MRH/CL	04 Mar 86

Dear Sirs

METHYLENE CHLORIDE (=DICHLOROMETHANE)

I am writing to you on behalf of the Methylene Chloride Workgroup of the European Council of Chemical Manufacturers' Federations (CEFIC) with regard to your 5 February 1986 'Request for Information' regarding methylene chloride.

This group has sponsored a 2-year program of research on the species differences in the mechanism of action and biological transformation of methylene chloride in an effort better to understand the marked species differences in tumorigenicity as evidenced by a number of long term bioassays in the rat, the hamster and the mouse in which only the mouse shows clear evidnece of a carcinogenic response - and this only at the high doses of the recent NTP inhalation bioassay, and yet not at the similar internal doses of the recent NCA ingestion (drinking water) bioassay. Further evidence suggestive of a species difference - or a dose-response difference, or both - is provided by the human epidemiology (particularly the 1985 and 1986 extensions of Friedlander's studies at Kodak, NY). This provides data which (while inevitably unable to "prove" a negative conclusion) makes any significant human risk a highly improbable hypothesis, and whose most probable explanation (by far) is the hypothesis of zero human risk.

Avenue Louise 250, Bte 72 B-1050 BRUXELLES Tél.: 640.20.95 Tlx : 62 498 Telefax : 640 1981

Our own studies are being conducted at the Central Toxicology Laboratory of Imperial Chemical Industries PLC in England, with external scientific monitoring and peer review b the European Chemical Industry Ecology & Toxicology Centre (ECETOC). The work will in due course be published in the scientific literature, and the laboratory studies are fully open to independent audit. The first stage of these studies has recently been completed, and copies of the three full final reports are enclosed; this work has also recently been presented at Toxicology Forum in Washington DC (February 1986) and at the Annual Meeting of the US Society of Toxicologists in New Orleans (March 1986); it has also been submitted to EPA, FDA, CPSC and OSHA.

This stage of our work has included a 10-day inhalation cytotoxicity study, DNA binding studies, and unscheduled DNA synthesis (UDS) studies (in vivo/ in vitro and in vitro) - in the B6C3F1 mouse and Fisher F344/N rat. We have found evidence of cytotoxicity to a specific cell type (the Clara cell) of the mouse lung, but not in the rat lung nor in mouse or rat liver. Under our experimental conditions we found no evidence for DNA-binding or UDS, strongly suggesting that under these conditions there is no interaction between methylene chloride or its metabolites and mammalian DNA. This would be consistent with a non-genotoxic action of methylene chloride, not necessarily because of "instantaneous detoxification of a carcinogen" (apparently the only rationale, among the many possible, considered in the Novermber 1985 California DHS carcinogen risk assessment guidelines) but more probably because (bearing in mind the existence of at least two independent metabolic pathways, at least one of which is saturable) no stable genotoxic intermediates were generated.

The second phase of our work, now in progress and expected to complete during the third quarter of 1986, is studying quantitatively the metabolic pathways involved in mouse, rat, hamster and man. Collection of the relevant pharmacokinetic data, and its incorporation into appropriate pharmacokinetic models, should allow us to establish and quantify interspecies differences in metabolism, the existence and level of any thresholds and, more generally, the shape of possible dose-response curves for comparison with animal bioassay findings, and with the findings of epidemiological studies.

It is our belief that this approach should assist the risk assessment process by allowing the use of experimentally-determined and scientifically valid dose-response relationships, rather than simplistic linear extrapolations between the high doses of animal bioassays and the much lower levels of human exposure, and the even greater extrapolation from mouse to man under circumstances where the mouse fails even to predict the bioassay response of such other rodents as the rat and the hamster.

Yours sincerely

DR M R HARRIS

Encs

DOCUMENTS ENCLOSED:

1. CEFIC submission to EPA. 20 September 1985. Interim report.
2. CEFIC submission to EPA. 13 December 1985. Interim report.
3. CEFIC Research Report No: CTL/P/1432. 10 Day Inhalation Toxicity Study.
4. CEFIC Research Report No: CTL/R/851. Interaction with Rat and Mouse Liver and Lung DNA *In Vivo*.
5. CEFIC Research Report No: CTL/P/1444. *In Vivo* and *In Vitro* UDS Studies.

METHYLENE CHLORIDE PRODUCERS ASSOCIATION

A CEFIC Sector Group

Conseil Europeen des
Federations de l'Industrie Chimique

European Council of Chemical
Manufacturer's Federations

Your Ref

Our Ref SG METHYLENE CHLORIDE

REPLIES TO:

M R Harris General Chemicals Business Group
Imperial Chemical Industries PLC
Mond Division
P O Box 13
RUNCORN Cheshire WA7 4QF

Telephone Runcorn (0928) 511344 (Direct)

William V Loscutoff
Chief of Toxic Pollutants Branch
Re: Methylene Chloride
California Air Resources Board
PO Box 2815
Sacramento
California 95812
USA

Your ref	Our ref	Date
	MRH/CL	08 Oct 86

Dear Sirs

METHYLENE CHLORIDE

We refer to our letter of 4 March 1986 with which we enclosed reports on the earlier phases of the research programme being conducted by us in Europe into species differences in response to methylene chloride, and their relevance to human health.

With our earlier letter we provided two interim and three final reports on the first phase of this work, in which no evidence could be found for any genotoxicity of methylene chloride in rats or mice - strongly suggesting that any quantitative carcinogenicity risk assessment could not simply extrapolate from high-dose bioassays to low occupational exposures, and would need to reflect cross-species differences.

We now have pleasure in submitting four final reports on the second phase of the CEFIC studies (Annexes 1 - 4) which describe the results of a study of S-phase hepatocyte induction in the mouse, of an evaluation of methylene chloride in the mouse micronucleus test, of *in vivo* studies on the pharmacokinetics and metabolism of methylene chloride in mouse and rat, and of *in vitro* studies on metabolism in rat, mouse, hamster and man.

Avenue Louise 250, Bte 72 B-1050 BRUXELLES Tel 640 20 95 Tlx 62 498 Telefax 640 1981

We believe that these latest studies from our research programme considerably add to the weight of evidence suggesting that methylene chloride does not express genotoxic effects in vivo in mammalian systems, and that the mouse is a quite inappropriate model for man in view of major differences in its metabolism of methylene chloride. Instead, the hamster would appear to be the most appropriate species for evaluating the human carcinogenic potential of methylene chloride. These results fit well with the observed absence of carcinogenicity in the hamster lifetime bioassay (Burek et al), and in the human epidemiology (Friedlander et al, as updated June 1986 with enhanced statistical power, and showing absence of dose-response).

We trust that this further new scientific information will assist the Air Resources Board and the Department of Health Services in assessing the level of any toxic hazard arising from methylene chloride. We believe that these results provide even greater confidence in the view that the recent NTP inhalation bioassay findings are without direct relevance for human health, and that methylene chloride does not pose a carcinogenic threat to humans.

We hope that Dr Trevor Green, who has been responsible for much of the work described in the enclosed reports, will be in California in November. If you feel that discussions at that time with scientists from DOHS or CARB would be helpful, perhaps you would let me know as soon as possible so that we may discuss dates. In any case, we will do our best to respond to any further queries you may have.

DR M R HARRIS
European Council of Chemical Manufacturers' Federations (CEFIC)
International Office for Chlorinated Solvents (BITSC)
Methylene Chloride Workgroup

Enclosed:

Annex 1. Methylene Chloride: An Evaluation in the Mouse Micronucleus Test
Report No: CTL/P/1603

Annex 2. Methylene Chloride: Induction of S-phase Hepatocytes in the Mouse after in vivo Exposure
Report No: CTL/R/885

Annex 3. Methylene Chloride: In vitro Metabolism in Rat, Mouse and Hamster Liver and Lung Fractions and in Human Liver Fractions
Report No: CTL/R/879

Annex 4. Methylene Chloride: In vivo Inhalation Pharmacokinetics and Metabolism in F344 Rats and B6C3F1 Mice
Report No: CTL/R/880

METHYLENE CHLORIDE PRODUCERS ASSOCIATION

A CEFIC Sector Group

Conseil Européen des
Fédérations de l'Industrie Chimique

European Council of Chemical
Manufacturer's Federations

Your Ref.

Our Ref. SG METHYLENE CHLORIDE

Replies to:

Dr M R Harris
Imperial Chemical Industries PLC
Mond Division
PO Box 13
The Heath
RUNCORN Cheshire WA7 4QF
ENGLAND

Tel: (0928) 511344 (Direct)

17th November 1986

William V Loscutoff
Chief of Toxic Pollutants Branch
Re: Methylene Chloride
California Air Resources Board
PO Box 2815
Sacramento
California 95812
USA

Dear Sirs

METHYLENE CHLORIDE - TOXICOLOGY REPORTS FROM CEFIC

We recently sent to you four reports on our toxicological investigations of methylene chloride, numbered and titled as follows:

Report No:	CTL/P/1603	... Evaluation in the Mouse Micronucleus Test
	CTL/R/879	... In Vitro Metabolism in Rat, Mouse and Hamster Liver and Lung Fractions and in Human Liver Fractions
	CTL/R/880	... In Vivo Inhalation Pharmacokinetics and Metabolism in F344 Rats and B6C3F1 Mice
	CTL/R/885	... Induction of S-phase Hepatocytes in the Mouse after In Vivo Exposure

Due to an administrative oversight, these reports were marked 'Confidential - not to be copied' on their title page. We would like to assure you that these reports are NOT confidential, contain no confidential business information, and are intended for placement on the public record for public comment and review.

We have also noted a calculation error in the data in Table 4 of Report No CTL/R/879 (In Vitro Metabolism) and enclose an audited correction sheet with the corresponding Quality Assurance Statement from the contracting Laboratory. The nature of the error is such that it does not in any way alter the conclusions in the text or the interpretation of the report.

We apologise for any inconvenience these errors may have caused.

Yours sincerely

DR M R HARRIS
Regulatory Affairs

Enc

METHYLENE CHLORIDE PRODUCERS ASSOCIATION

A CEFIC Sector Group

Conseil Européen des
Fédérations de l'Industrie Chimique

European Council of Chemical
Manufacturer's Federations

Your Ref.

Our Ref SG METHYLENE CHLORIDE

Replies to:

Dr M R Harris
Imperial Chemical Industries PLC
Chemicals & Polymers Group
PO Box 13
The Heath
RUNCORN Cheshire WA7 4QF
ENGLAND

Tel: (0928) 511344 (Direct)

8th May, 1987

METHYLENE CHLORIDE (DICHLOROMETHANE). SPECIES DIFFERENCES IN METABOLISM.

Further to our earlier submissions, we are pleased to enclose an interim statement giving the latest results of metabolic studies conducted on our behalf at the Central Toxicology Laboratory of ICI in England, and confirmed by parallel independent studies by the Mammalian and Environmental Toxicology Laboratory of Dow Chemical Company in the USA.

We expect to report in more detail on our own further studies by means of a further interim submission in early June in order that the Science Advisory Board may have as much information as possible available for the June meeting of the Halogenated Solvents Subcommittee. A full report should be available in July/August 1987 and should contain more detailed metabolic and pharmacokinetic findings.

Dr M R Harris
Chairman, Methylene Chloride Workgroup
Bureau International des Solvants Chlores (BITSC), CEFIC

Avenue Louise 250, Bte 72 B-1050 BRUXELLES Tél.: 640.20.95 Tlx : 62 498 Telefax : 640 1981

METHYLENE CHLORIDE PRODUCERS ASSOCIATIO

A CEFIC Sector Group

Conseil Européen des
Fédérations de l'Industrie Chimique

European Council of Chemical
Manufacturer's Federations

Your Ref.

Our Ref. SG METHYLENE CHLORIDE

Replies to:

Dr M R Harris
Imperial Chemical Industries PLC
Chemicals & Polymers Group
PO Box 13
The Heath
RUNCORN Cheshire WA7 4QF
ENGLAND

Tel: (0928) 511344 (Direct)

15th July, 1987

Dr W V Loscutoff
Chief of Toxic Pollutants Branch
California Air Resources Board
P O Box 2815
Sacramento
California 95812
USA

Dear Mr Loscutoff

METHYLENE CHLORIDE (DICHLOROMETHANE):

NEW RESULTS FROM RESEARCH INTO SPECIES DIFFERENCES IN TOXICOLOGY:

Please find attached ECETOC Statement No. 4 (June 1987) being a further submission of results from ongoing research sponsored by CEFIC and conducted at the Central Toxicology Laboratory of ICI in England.

The results further extend and further quantify our understanding of the marked cross-dose and cross-species differences in the toxicology of methylene chloride in three rodent species and in man.

Full reports of these studies will be available in October 1987.

Yours sincerely

pp

Dr M R Harris
Methylene Chloride Workgroup
Bureau International Technique des Solvants Chlores
Conseil Europeen des Federations de l'Industrie Chimique

Encl

Avenue Louise 250, Bte 72 B-1050 BRUXELLES Tél.: 640.20.95 Tlx : 62 498 Telefax : 640 1981

E. I. DU PONT DE NEMOURS & CO. (INC.)
WILMINGTON, DELAWARE 19898

MARKETING COMMUNICATIONS DEPARTMENT

February 18, 1986

Mr. Peter D. Venturini
State of California
Air Resources Board
P.O. Box 2815
Sacramento, CA 95812

Dear Mr. Venturini:

Thank you for your recent correspondence requesting information concerning methylene chloride.

The Du Pont Company is not currently engaged in the manufacture or supply of this item.

Listed below is the name and address of the firm indicated as manufacturer or supplier of the product involved.

Dow Chemical USA
2020 Dow Center
Midland, MI 48640
517-636-1000

We acknowledge and appreciate your interest in our Company.

Product Information Center
800-441-7515

Chevron

Chevron Environmental Health Center, Inc.
A Chevron Research Company Subsidiary
15299 San Pablo Avenue, Richmond, California
Mail Address P.O. Box 4054, Richmond, CA 94804

R. D. Cavalli
Manager
Product Evaluation

February 24, 1986

Methylene Chloride

William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Board
P.O. Box 2875
Sacramento, California 95812

Dear Mr. Loscutoff:

As per your request, in accordance with Health and Safety Code Sections 39650, et seq., we have reviewed our files on the health effects of methylene chloride. We have no relevant "in-house" data on methylene chloride, but feel the following references may be useful additions to the bibliography for the Department of Health Services:

1. Heppel, L. A., Neal, P. A., Perrin, T. L., Orr, M. L., Porterfield: Toxicology of Dichloromethane (Methylene Chloride). I. Studies on Effects of Daily Inhalation. J. Ind. Hyg. Toxicol. 26: 8-16, 1944.

2. Heppel, L. A., Neal, P. A.: Toxicology of Dichloromehtane (Methylene Chloride). II. Its Effect Upon Running Activity in the Male Rat. J. Ind. Hyg. Toxicol. 26: 17-21, 1944.

Thank you for the opportunity to contribute to the review of candidate toxic air contaminants.

Sincerely,

RD Cavalli /GFSM

New York State Department of Environmental Conservation
50 Wolf Road, Albany, New York 12233-0001

Henry G. Williams
Commissioner

March 7, 1986

RECEIVED

MAR 11 1986

Stationary Source
Division
Air Resources Board

Mr. Peter Venturini
Chief
Stationary Source Division
State of California
Air Resources Board
1102 Q Street
P. O. Box 2815
Sacramento, California 95812

Dear Mr. Venturini:

This is in response to your letter of February 5, 1986 in which you requested information on the health effects of methylene chloride. At this time, we are conducting a quantitative risk assessment by applying statistical models to the bioassay data obtained from the inhalation study completed by the National Toxicology Program (NTP) in 1985. In addition, we will be completing a search of the same references which were included with your letter.

When we have completed this risk assessment, we will be glad to send you a copy.

Sincerely,

Virginia M. Rest

Virginia M. Rest
Environmental Chemist
Section of Toxics Assessment
Bureau of Air Toxics

VMR:cb

BASIC PRODUCTS GROUP
CHLOR-ALKALI PHOSPHORUS
& SULFURIC PRODUCTS
DIVISIONS

Stauffer Chemical Company
636 California St./San Francisco, CA 94108/Tel. (415) 544-9311/Cable "Stauffer"

REPLY TO:
P. O. Box 7766
San Francisco, CA 94120

March 3, 1986

William V. Loscutoff, Chief
Toxic Pollutants Branch
RE: Methylene Chloride
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

Dear Mr. Loscutoff:

Per your request, attached please find a copy of our Product Safety Information Sheet for Methylene Chloride.

Also, please be advised that as of March 1, 1986, Stauffer Chemical Company is no longer in the Methylene Chloride business.

Sincerely,

W. J. Meier
Senior Technical Service Representative
Basic Chemicals Division

WJM:el
enclosure

Product Safety Information

METHYLENE CHLORIDE

This Product Safety Information Sheet is principally directed to managerial, safety, hygiene and medical personnel. The description of physical, chemical and toxicological properties and handling advice is based on experimental results and past experience. It is intended as a starting point for the development of health and safety procedures.

Synonyms: Dichloromethane; Methylene dichloride
CAS Registry Number: 75-09-2

I. PHYSICAL AND CHEMICAL PROPERTIES

Formula
CH_2Cl_2
Formula Weight
84.94
Physical State/Description
Colorless volatile liquid at 68°F (20°C), 14.7 psia
Autoignition Temperature
1224°F (662°C)
Boiling Point
104°F (40°C)
Density
11 lbs/gallon at 68°F (20°C)
Evaporation Rate
1.47 (Carbon tetrachloride = 1)
Explosive Limits In Pure Oxygen
LEL: 15.5%; UEL: 66.4%
Flammability Limits In Air
13.9 to 19.1 [% volume at 212°F (100°C)]
Freezing Point
-142°F (-96.7°C)
Miscibility
Miscible with alcohol and ether
Odor
Penetrating, ether-like, pleasantly aromatic, sweet odor
pH
Slightly alkaline (water extract)
Solubility
Sparingly soluble in water
[1.99 g/100g in water at 68°F (20°C)]
Specific Gravity
1.326 at 68°F/68°F (20°C/20°C)
Vapor Pressure
140 mmHg at 32°F (0°C)
350 mmHg at 68°F (20°C)
700 mmHg at 100°F (37.7°C)
Viscosity
0.43 cp at 68°F (20°C)

IN CASE OF SUSPECTED POISONING, REFER TO THE PROCEDURE AND EMERGENCY CONTACTS IN SECTION VIII: FIRST AID.

IN CASE OF SPILLAGE, REFER TO THE PROCEDURE AND EMERGENCY CONTACTS IN SECTION X: SPILL HANDLING OR CALL (CHEMTREC) (800) 424-9300.

II. CHEMICAL REACTIVITY

Does not undergo hazardous polymerization. However, a serious chemical reaction, with the possibility of explosion, could result if halogenated hydrocarbon solvents are used in pressurizable fluid systems having aluminum or galvanized wetted parts. Prolonged exposure to water at elevated temperatures (140°F/60°C) may cause noticeable hydrolysis. May react violently or explode upon contact with alkali or chemically active metals such as finely powdered aluminum, magnesium, potassium and/or sodium.

III. STABILITY

Stable at ambient temperatures and atmospheric pressure. However, exposure to high temperature sources (such as open flame and welding arcs) causes thermal-oxidative decomposition yielding toxic phosgene gas and corrosive hydrogen chloride.

IV. FIRE HAZARD

Methylene chloride does not have a measurable flash point by conventional test methods. It is not considered flammable but forms flammable vapor/air mixtures at approximately 212°F (100°C) or higher. Under fire conditions, decomposes to form toxic phosgene gas and corrosive hydrogen chloride.

V. FIREFIGHTING TECHNIQUE

Vapors are irritating to the respiratory tract and may cause breathing difficulty and pulmonary edema. Symptoms may be delayed several hours or longer depending upon the extent of exposure.

As in any fire, prevent human exposure to fire, smoke, fumes or products of combustion. Evacuate nonessential personnel from the fire area. Firefighters should wear full-face, self-contained breathing apparatus and protective clothing.

Use standard firefighting techniques to extinguish fires involving this material—use water spray, dry chemicals or carbon dioxide.

If not leaking, use a water spray to keep fire-exposed containers cool to prevent rupture due to excessive heat. High pressure water hose may spread product from broken containers increasing contamination or fire hazard.

VI. HUMAN HEALTH

WARNING: Vapor and liquid may be harmful if inhaled, swallowed, or absorbed by skin. Avoid prolonged or repeated breathing of vapor. May cause skin and eye irritation. Avoid contact with skin, eyes, and clothing.

The primary route of entry for methylene chloride is inhalation.

Inhalation of large amounts of the vapor may cause nausea, chills, headache, lightheadedness, drowsiness, and irritation of the respiratory tract. Continued overex-

posure may produce unconsciousness, kidney and lung damage, and death.

Eye irritation and blurred vision may result from eye contact by the liquid or large quantities of the vapor.

Prolonged skin contact with the liquid may cause burns. Repeated skin exposures may produce dermatitis.

LONG TERM EXPOSURE: An epidemiological study performed on a large group of male workers at an Eastman Kodak facility in New York, who were continuously exposed to estimated TWA exposures of 30 - 125 ppm of methylene chloride for up to 30 years, has been reported. There was no increase in mortality among exposed workers as compared to industrial controls and the general New York State male population. (1)

VII. TOXICOLOGY

Ingestion

The acute oral LD50 is 2,710 mg/kg in male rats and 2,330 mg/kg in female rats. A single oral dose of 2,150 mg/kg produced mild depression and 20 percent mortality in male rats, and produced moderate to severe depression, tremors and 40 percent mortality in female rats. A single oral dose of 4,640 mg/kg resulted in dyspnea, ataxia, and narcosis in female rats and 100% mortality in male and female rats.

Skin Contact

The acute dermal LD50 is greater than 4,640 mg/kg in rabbits. A single dermal application of 4,640 mg/kg did not produce signs of toxicity in male or female rabbits. Local effects included a mild erythema and moderate edema.

Mild to moderate irritant to rabbit skin following a 4-hour exposure.

Eye Contact

A single ocular dose of 0.1 mL produced lacrimation, inflammation, conjunctival edema, and an increased corneal thickness (reversible). (2)

Inhalation

The acute inhalation LC50 is greater than 19.5 mg/L (nominal concentration) in both male and female rats. A single 1-hour inhalation exposure of 19.5 mg/L (nominal concentration) produced slight depression, moderate ataxia, and ocular protrusion. The acute inhalation LC50 in mice is approximately 14,400 - 17,400 ppm. Seven hour exposures to doses ranging from 13,000 - 17,000 ppm produced ataxia, labored respiration, muscular twitching, and narcosis. (3)

Monkeys, dogs, rabbits, guinea pigs and rats exposed to 500 ppm for 8 hour/day, 5 days/week, for 15 weeks showed 20% mortality (in rats), and a slight increase in eosinophils (rabbits). (3)

Monkeys, dogs, rats, and mice were continuously exposed to 25 or 100 ppm for 100 days. No overt signs of stress were observed. The exposure produced: histopathological effects in mouse livers (100 ppm) and rat kidneys (25 and 100 ppm); no significant findings in hematology, clinical chemistry or histopathology in dogs and monkeys; and significantly increased carboxyhemoglobin in dogs and monkeys (monkeys 100 and 25 ppm, dogs 100 ppm). (3)

Rats and hamsters were exposed by inhalation to 0, 500, 1,500 or 3,500 ppm of methylene chloride for 6 hours per day, 5 days a week for 2 years. No organ-specific toxicity was observed in hamsters. Carboxyhemoglobin levels were elevated in hamsters and rats at all dose levels, but this effect was not cumulative. (4)

Histopathological effects in the liver were observed in male and female rats at all dose levels and considered to be exposure-related. Despite these effects, there was no increase in neoplastic (hyperplastic) liver nodules and no increase in hepatocellular carcinomas. (4)

Increased total numbers of benign mammary tumors were seen in male and female rats, but no increase in malignant mammary tumors was observed. There were no significant lung tumor findings in any exposed group compared to the controls. (4)

Male rats in the 3,500 ppm dose group exhibited a significant increase in sarcomas in or around the salivary glands. A significant increase in this finding was not observed in males exposed at 500 or 1,500 ppm or any of the exposed females. (4)

In a second study, male and female rats were exposed to 0, 50, 200, or 500 ppm for 6 hrs/day, 5 days/week for 2 years. Additionally, one group of females was exposed at 500 ppm for the first 12 months only, and another group for the second 12 months only. (5)

A significant increase in histopathological effects in the liver was observed in females exposed to 500 ppm for 2 years and to 500 ppm for the first 12 months. (5)

Mutagenicity

Methylene chloride was examined for mutagenic activity in *in vitro* microbial assays, with and without metabolic activation, using the TA-100 and TA-98 strain of *Salmonella typhimurium* as the indicator organism. The compound demonstrated mutagenic activity in both assays. (6)

Methylene chloride did not induce chromosomal aberrations in a rat bone marrow assay. (4)

Methylene chloride induced cellular transformation in Fischer rat embryo cells. (7)

T-4054, T-4171, T-5528

VIII. FIRST AID

CALL A POISON CENTER OR
A PHYSICIAN IMMEDIATELY.

If a known exposure occurs or is suspected, immediately start the recommended procedures below. Simultaneously contact a Poison Center, a physician or the nearest hospital. Inform the person contacted of the type and extent of exposure, describe the victim's symptoms, and follow the advice given.

NOTE TO PHYSICIAN

Methylene chloride is metabolized to carbon monoxide and carbon dioxide. The resultant elevation of carboxyhemoglobin levels is of short duration (e.g. usually less

(1) J. Occ. Med. 20 (10):657 (1978).
(2) Toxicol. 6:173-187 (1976).
(3) HEW (NIOSH) Publication No. 76-138.
(4) Burek, J. D. et. al (1980) Methylene Chloride: "A Two-Year Inhalation Toxicity and Oncogenicity Study in Rats and Hamsters." Final Report Issued December 31, 1980 by Dow Chemical, USA.
(5) Nitschke, K. D. et. al (1982) Methylene Chloride: "A Two-Year Toxicity and Oncogenicity Study." Final Report Issued October 11, 1982 by Dow Chemical, USA.
(6) Mut.Res. 56:245-248 (1978)
(7) In Vitro 14:290-293 (1978)

than 48 hours) unless overexposure is prolonged. Inhalation of large amounts of methylene chloride may cause pulmonary edema and could be fatal. Exposure to high concentrations of methylene chloride may cause depression of the central nervous system.

FOR ADDITIONAL MEDICAL OR TOXICOLOGICAL INFORMATION, CALL COLLECT, DAY OR NIGHT, STAUFFER CHEMICAL COMPANY (203) 225-6602 OR CHEMTREC (800) 424-9300.

Ingestion
If swallowed, immediately give several glasses of water but *do not* induce vomiting. If vomiting does occur, give fluids again. Have a physician determine if condition of patient will permit induction of vomiting or evacuation of stomach. Do not give anything by mouth to an unconscious or convulsing person.

Skin Contact
Immediately flush all affected areas with large amounts of water for at least 15 minutes while removing any contaminated clothing and shoes. Do not attempt to neutralize with chemical agents. Get medical attention immediately. Wash clothing before reuse.

Eye Contact
Immediately flush the eyes with large quantities of running water for a minimum of 15 minutes. Hold the eyelids apart during the flushing to ensure rinsing of the entire surface of the eye and lids with water. Do not attempt to neutralize with chemical agents. Obtain medical attention as soon as possible. Oils or ointments should not be used. Continue the flushing for an additional 15 minutes if the physician is not immediately available.

Inhalation
Remove from contaminated atmosphere. Seek medical attention if respiratory irritation occurs. If the breathing becomes difficult, oxygen may be delivered from a demand-type or continuous flow inhaler, preferably with a physician's advice. If not breathing, give artificial respiration, preferably mouth-to-mouth. Get medical attention.

IX. INDUSTRIAL HYGIENE

Ingestion
All food should be kept in a separate area away from the storage/use location. Eating, drinking and smoking should be prohibited in areas where there is a potential for significant exposure to this material. Before eating, hands and face should be thoroughly washed.

Skin Contact
Skin contact with liquid or its aerosol should be prevented through the use of suitable protective clothing, gloves and footwear selected with regard for use condition exposure potential.

Eye Contact
Eye contact with liquid or its aerosol should be prevented through the use of chemical safety glasses, goggles or a face shield selected with regard for use condition exposure potential.

Inhalation
If use conditions generate airborne liquid, aerosol or vapor handle this material only in an open (e.g., outdoor) or well ventilated area. Where adequate ventilation is not available, use NIOSH-approved organic vapor respirators to reduce exposure. Where exposure potential under the use conditions necessitates a higher level of protection, use a positive-pressure, air-supplied respirator.

Exposure Limits
The Federal OSHA Permissible Exposure Limit (PEL) is an 8-hour, time-weighted average of 500 ppm (1,700 mg/m^3) and a ceiling concentration of 1,000 ppm for methylene chloride. (4)

The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a Threshold Limit Value (TLV) of 100 ppm (360 mg/m^3) as an 8-hour time-weighted average, and a Short Term Exposure Limit (STEL) of 500 ppm (1,700 mg/m^3) for methylene chloride. (5)

X. SPILL HANDLING

Make sure all personnel involved in the spill cleanup follow good industrial hygiene practices (refer to SECTION IX: INDUSTRIAL HYGIENE). Any person entering a significant spill area or an unknown concentration of a gas or vapor, should wear a positive-pressure, self-contained breathing apparatus or a positive-pressure, supplied-air respirator with escape pack.

Small spills can be handled routinely. Use adequate ventilation and wear a respirator to prevent inhalation exposure. Wear protective clothing to prevent skin and eye contact. Use the following procedures:

Evacuate spill area and remove sources of combustion or extreme heat. Ventilate the area and let small spills evaporate. Somewhat larger spills should be contained and recovered where possible. Mop up spilled methylene chloride or adsorb with a suitable adsorbent such as clay, sawdust or kitty litter. Reclaim waste solvent by distillation procedures or offer for disposal to a licensed hydrocarbon solvent reclaimer.

Large spills should be handled according to a predetermined plan. For assistance in developing a plan, contact Stauffer Chemical Company, Westport, CT 06881.

IN CASE OF SPILL EMERGENCY, DAY OR NIGHT, CALL (800) 424-9300 CHEMTREC.

XI. CORROSIVITY TO MATERIALS OF CONSTRUCTION

In the absence of contamination by water or moisture, methylene chloride is not corrosive to common materials such as copper, iron or stainless steel. In contact with water or moisture, particularly at elevated temperatures, it can be corrosive. Methylene chloride may soften or dissolve certain plastics and rubbers. Avoid contact with alkali or chemically active metals because an explosion may occur (See SECTION II: CHEMICAL REACTIVITY).

(4) 29 CFR 1910.1000

(5) The American Conference of Governmental Industrial Hygienists (ACGIH). 1982. *Threshold Limit Values for chemical substances and physical agents in the workroom environment with intended changes for 1982.* ACGIH: Cincinnati, Ohio.

XII. STORAGE REQUIREMENTS

Containers should be stored in a cool, dry, well ventilated area away from flammable materials and sources of heat or flame. Store away from foodstuffs or animal feed. Exercise due caution to prevent damage to or leakage from the container.

Avoid airborne concentration buildup. No smoking where vapors of this material are present. Open containers with caution.

When methylene chloride vapors are drawn into the combustion chamber of a space heater, even at low levels, severe corrosion damage to the heater can occur.

XIII. DISPOSAL OF UNUSED MATERIAL

Material that cannot be used or chemically reprocessed should be disposed of at an approved facility in accordance with any applicable regulations under the Resource Conservation and Recovery Act.

NOTE: State and local regulations may be more stringent than Federal.

Contact the nearest Stauffer Sales Office for assistance in disposing of unused material. Waste material can be sent to a licensed hydrocarbon solvent reclaimer.

XIV. DISPOSAL OF CONTAINER

Dispose of empty containers according to any applicable regulations under the Resource Conservation and Recovery Act.

NOTE: State and local regulations may be more stringent than Federal.

XV. ENVIRONMENTAL PRECAUTIONS

Avoid runoff to sewers.

PACIFIC GAS AND ELECTRIC COMPANY

PG&E 77 BEALE STREET • SAN FRANCISCO, CALIFORNIA 94106 • (415) 781-4211 • TWX 910-372-6587

June 4, 1986

Mr. William V. Loscutoff, Chief
Toxic Pollutants Branch
Re: Methylene Chloride
California Air Resources Board
P.O. Box 2815
Sacramento, California 95812

Dear Mr. Loscutoff:

Request for Public Health
Information Regarding Methylene Chloride

Pacific Gas and Electric Company received your February 5, 1986 request for additional public health information regarding Methylene Chloride. We have reviewed the bibliography attached to your request and concluded that we are unaware of any additional information which would be of use to you.

When the risk assessment report becomes available, please send me a copy.

Sincerely,

J. F. McKenzie

APPENDIX V

HEALTH EFFECTS REQUEST TO DHS AND LETTER OF RESPONSE

ATTACHMENT I

HSIA HALOGENATED SOLVENTS INDUSTRY ALLIANCE

2315 M Street, N.W., Third Floor, Washington, D.C. 20037 • (202) 223-5890

March 27, 1986

Mr. William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Branch
P.O. Box 2815
Sacramento, CA 95812

Re: Methylene Chloride

Dear Mr. Loscutoff:

We thank you for providing us the opportunity to submit health information on methylene chloride. We are enclosing a variety of recent documents and articles which were not included in your list of references. Please note that the last two references listed are not enclosed. They are currently being cleared for outside release and should be sent within two weeks.

HSIA understands that this information will be used by the State Department of Health Services in its process of considering all available scientific data in its evaluation of health effects and recommendation as to whether or not methylene chloride should be determined to be a toxic air contaminant.

A toxic air contaminant is defined in AB 1807 as:

> An air pollutant which may cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health.

HSIA believes that methylene chloride does not cause adverse health effects when used according to current industrial hygiene guidelines or labeled instructions. Furthermore, there is no scientific evidence to indicate that ambient concentrations of methylene chloride cause or contribute to an increase in mortality or an increase in serious illness, or which may pose a present or potential hazard to human health. HSIA believes that adequate scientific evidence exists to determine that methylene chloride does not meet the above definition of a toxic air contaminant and should not be identified as one.

We submit the following scientific information as the basis for our conclusion that methylene chloride should not be identified as a toxic air contaminant.

1. Two well-conducted epidemiologic studies have been completed on worker populations exposed to methylene chloride. Neither study indicated a human cancer risk associated with methylene chloride exposure. The most definitive study compare the mortality rate of over 1,000 employees with identified methylene chloride exposure to an unexposed worker population. The findings of this study indicate that workers to methylene chloride for a minimum of 20 years and observed over 20 additional years actually had a decreased incidence of cancer when compared to the New York State control population.

   The other epidemiologic study of methylene chloride examined the health and mortality of over 1200 employees exposed to a mixture of methylene chloride, ethanol, and acetone in a fiber production plant. The study showed no excess mortality cancer in the workers exposed to methylene chloride, even though exposures had ranged up to 475 parts per million and over 300 of them had been followed at least 17-1/2 years after exposure. This study is highly relevant to an understanding of the health risk posed by methylene chloride.

2. The only sites in which methylene chloride has produced tumors are those sites in experimental rodents where the tumors occur spontaneously in unexposed animals (mouse lung and liver tumors and benign mammary gland tumors in rats with no progression to malignancy). The only exception is a low but statistically significant incidence of ventral neck region tumors in male rats only in one study. This response was reviewed and its relevance severely questioned by the U.S. EPA Science Advisory Board and at the Nutrition Foundation Food Solvents Workshop on Methylene Chloride in 1984. Most importantly and of extreme toxicological significance is the fact that the ventral neck region tumor response was not repeatable in the NTP bioassay in rats in any other species evaluated (mouse and hamster).

3. Methylene chloride has been evaluated in numerous short-term in vitro tests, from microorganisms to mammalian cells in culture, as well as in whole animal assays to determine its genotoxic potential. Aside from positive activity in certain microorganisms (primarily bacteria), results in mammalian cells and whole animals, have, for the most part, been negative. A genotoxic component, if present at all in exposed animals is likely to be very weak to nil and not a significant factor in the toxicity of methylene chloride. Thus the principle of practical no-effect-levels should apply in assessing risk for humans.

4. Mechanistic studies have been conducted which provide plausible hypotheses for the observed enhancement of spontaneous tumors in animals exposed to high concentrations of methylene chloride (mouse lung/liver; cytotoxicity/physiological stimulation: rat benign mammary gland; elevated prolactin levels). HSIA believes that humans are not exposed to levels of methylene chloride in the ambient environment which could cause is chain of events to occur. Furthermore, development of a physiologically-based pharmacokinetic model for methylene chloride has confirmed that markedly lower tissue levels of bioactive metabolites of methylene chloride (lower internal dose) would be found in humans than in experimental animals exposed to comparable external concentrations of methylene chloride.

To summarize, HSIA believes that methylene chloride should not be identified as a toxic air contaminant. We have enclosed additional pertinent references to support this belief. In addition we offer our cooperation in answering any questions which might arise in this review of methylene chloride.

Please feel free to call me at (202) 223-5890.

Sincerely yours,

Paul A. Cammer

Paul Cammer, Ph.D.
Executive Director

Enclosure

ADDITIONAL REFERENCES SUBMITTED TO THE CALIFORNIA AIR RESOURCES BOARD ON METHYLENE CHLORIDE

Comments of HSIA before the U.S. Environmental Protection Agency, Docket No. OPTS-62045: Methylene Chloride; Initiation of Regulatory Investigation, December 16, 1985.

Comments of HSIA before the U.S. Environmental Protection Agency, Regarding Docket No 1 OPTS-48503: Methylene Chloride; Initiation of Accelerated Review Under Section 4(f) of the Toxic Substance Control Act, July 15, 1985.

Letter of July 30, 1985 to Lee M. Thomas from Drs. Griesemer and Nelson, concerning the HAD Addendum.

Anderson, M. E., Clewell, H. J. II, Gargas, M. J., Smith, F. A., and Reitz, R. H.,Physiologically-Based Pharmacokinetics and the Risk Assessment Process for Methylene Chloride, Toxicol.Appl.Pharmacol. (submitted for publication, Jan 1986).

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Thilagar, A. K., Kumaroo, P. V., Clarke, J. J., Kott, S., Back, A. M. and Kirby, P. E., Induction of Chromosome Damage by Dichloromethane in Cultured Human Peripherial Lymphocytes, CHO Cells and Mouse Lymphoma L5178Y Cells, Environ. Mutagenesis 6:422 (1984).

Dutton, D. R. and Bowden, G. T., Indirect Induction of a Plastogenic Effect on Epidermal Cells by a Tumor Promoter, Carcinogenesis 6:1279-1284 (1985).

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Welsch, C. W. and Nagaswa, H. (1977). Prolactin and murine mammary tumorigenesis: a review. Cancer Research 37, 951-963.

Letter of July 18, 1984 to William D. Ruckelshaus from Herschel E. Griffin and Norton Nelson.

** Breslein, W. J. and Landry, T. D. (1986). Methylene chloride: effects on estrous cycling and serum prolactin in Sprague-Dawley rats. Report of the Dow Chemical Co., Midland, MI 48640.

** Schuman, A. M. (1986). Perspective on the genetic toxicology data base for methylene chloride. The Dow Chemical Co., Midland, MI 48640.

** Not enclosed. Currently being cleared for outside release.

METHYLENE CHLORIDE PRODUCERS ASSOCIATION

A CEFIC Sector Group

Conseil Européen des
Fédérations de l'Industrie Chimique

European Council of Chemical
Manufacturer's Federations

Your Ref.

Our Ref. SG METHYLENE CHLORIDE

REPLIES TO: Dr M R Harris
Regulatory Affairs
Imperial Chemical Industries PLC
Mond Division, PO Box 13
The Heath, Runcorn, WA7 4QF
CHESHIRE, England

William V Loscutoff
Chief of Toxic Pollutants Branch
Re: Methylene Chloride
California Air Resources Board
PO Box 2815
Sacramento
California 95812
USA

Your ref	Our ref	Date
	MRH/CL	04 Mar 86

Dear Sirs

METEYLENE CHLORIDE (=DICHLOROMETHANE)

I am writing to you on behalf of the Methylene Chloride Workgroup of the European Council of Chemical Manufacturers' Federations (CEFIC) with regard to your 5 February 1986 'Request for Information' regarding methylene chloride.

This group has sponsored a 2-year program of research on the species differences in the mechanism of action and biological transformation of methylene chloride in an effort better to understand the marked species differences in tumorigenicity as evidenced by a number of long term bioassays in the rat, the hamster and the mouse in which only the mouse shows clear evidnece of a carcinogenic response - and this only at the high doses of the recent NTP inhalation bioassay, and yet not at the similar internal doses of the recent NCA ingestion (drinking water) bioassay. Further evidence suggestive of a species difference - or a dose-response difference, or both - is provided by the human epidemiology (particularly the 1985 and 1986 extensions of Friedlander's studies at Kodak, NY). This provides data which (while ineyitably unable to "prove" a negative conclusion) makes any significant human risk a highly improbable hypothesis, and whose most probable explanation (by far) is the hypothesis of zero human risk.

Our own studies are being conducted at the Central Toxicology Laboratory of Imperial Chemical Industries PLC in England, with external scientific monitoring and peer review b the European Chemical Industry Ecology & Toxicology Centre (ECETOC). The work will in due course be published in the scientific literature, and the laboratory studies are fully open to independent audit. The first stage of these studies has recently been completed, and copies of the three full final reports are enclosed; this work has also recently been presented at Toxicology Forum in Washington DC (February 1986) and at the Annual Meeting of the US Society of Toxicologists in New Orleans (March 1986); it has also been submitted to EPA, FDA, CPSC and OSHA.

This stage of our work has included a 10-day inhalation cytotoxicity study, DNA binding studies, and unscheduled DNA synthesis (UDS) studies (in vivo/ in vitro and in vitro) - in the B6C3F1 mouse and Fisher F344/N rat. We have found evidence of cytotoxicity to a specific cell type (the Clara cell) of the mouse lung, but not in the rat lung nor in mouse or rat liver. Under our experimental conditions we found no evidence for DNA-binding or UDS, strongly suggesting that under these conditions there is no interaction between methylene chloride or its metabolites and mammalian DNA. This would be consistent with a non-genotoxic action of methylene chloride, not necessarily because of "instantaneous detoxification of a carcinogen" (apparently the only rationale, among the many possible, considered in the November 1985 California DHS carcinogen risk assessment guidelines) but more probably because (bearing in mind the existence of at least two independent metabolic pathways, at least one of which is saturable) no stable genotoxic intermediates were generated.

The second phase of our work, now in progress and expected to complete during the third quarter of 1986, is studying quantitatively the metabolic pathways involved in mouse, rat, hamster and man. Collection of the relevant pharmacokinetic data, and its incorporation into appropriate pharmacokinetic models, should allow us to establish and quantify interspecies differences in metabolism, the existence and level of any thresholds and, more generally, the shape of possible dose-response curves for comparison with animal bioassay findings, and with the findings of epidemiological studies.

It is our belief that this approach should assist the risk assessment process by allowing the use of experimentally-determined and scientifically valid dose-response relationships, rather than simplistic linear extrapolations between the high doses of animal bioassays and the much lower levels of human exposure, and the even greater extrapolation from mouse to man under circumstances where the mouse fails even to predict the bioassay response of such other rodents as the rat and the hamster.

Yours sincerely

DR M R HARRIS

Encs

DOCUMENTS ENCLOSED:

1. CEFIC submission to EPA. 20 September 1985. Interim report.

2. CEFIC submission to EPA. 13 December 1985. Interim report.

3. CEFIC Research Report No: CTL/P/1432. 10 Day Inhalation Toxicity Study.

4. CEFIC Research Report No: CTL/R/851. Interaction with Rat and Mouse Liver and Lung DNA In Vivo.

5. CEFIC Research Report No: CTL/P/1444. In Vivo and In Vitro UDS Studies.

BASIC PRODUCTS GROUP
CHLOR-ALKALI PHOSPHORUS
& SULFURIC PRODUCTS
DIVISIONS

Stauffer Chemical Company
636 California St./San Francisco, CA 94108/Tel. (415) 544-9311/Cable "Stauffer"

REPLY TO:
P. O. Box 7766
San Francisco, CA 94120

March 3, 1986

William V. Loscutoff, Chief
Toxic Pollutants Branch
RE: Methylene Chloride
California Air Resources Board
P. O. Box 2815
Sacramento, CA 95812

Dear Mr. Loscutoff:

Per your request, attached please find a copy of our Product Safety Information Sheet for Methylene Chloride.

Also, please be advised that as of March 1, 1986, Stauffer Chemical Company is no longer in the Methylene Chloride business.

Sincerely,

W. J. Meier
Senior Technical Service Representative
Basic Chemicals Division

WJM:el
enclosure

Product Safety Information

METHYLENE CHLORIDE

This Product Safety Information Sheet is principally directed to managerial, safety, hygiene and medical personnel. The description of physical, chemical and toxicological properties and handling advice is based on experimental results and past experience. It is intended as a starting point for the development of health and safety procedures.

Synonyms: Dichloromethane; Methylene dichloride
CAS Registry Number: 75-09-2

I. PHYSICAL AND CHEMICAL PROPERTIES

Formula
CH_2Cl_2
Formula Weight
84.94
Physical State/Description
Colorless volatile liquid at 68°F (20°C), 14.7 psia
Autoignition Temperature
1224°F (662°C)
Boiling Point
104°F (40°C)
Density
11 lbs/gallon at 68°F (20°C)
Evaporation Rate
1.47 (Carbon tetrachloride = 1)
Explosive Limits In Pure Oxygen
LEL: 15.5%; UEL: 66.4%
Flammability Limits In Air
15.9 to 19.1 [% volume at 212°F (100°C)]
Freezing Point
-142°F (-96.7°C)
Miscibility
Miscible with alcohol and ether
Odor
Penetrating, ether-like, pleasantly aromatic, sweet odor
pH
Slightly alkaline (water extract)
Solubility
Sparingly soluble in water
[1.96 g/100g in water at 68°F (20°C)]
Specific Gravity
1.326 at 68°F/68°F (20°C/20°C)
Vapor Pressure
140 mmHg at 32°F (0°C)
350 mmHg at 68°F (20°C)
700 mmHg at 100°F (37.7°C)
Viscosity
0.43 cp at 68°F (20°C)

IN CASE OF SUSPECTED POISONING, REFER TO THE PROCEDURE AND EMERGENCY CONTACTS IN SECTION VIII: FIRST AID.

IN CASE OF SPILLAGE, REFER TO THE PROCEDURE AND EMERGENCY CONTACTS IN SECTION X: SPILL HANDLING OR CALL (CHEMTREC) (800) 424-9300.

II. CHEMICAL REACTIVITY

Does not undergo hazardous polymerization. However, a serious chemical reaction, with the possibility of explosion, could result if halogenated hydrocarbon solvents are used in pressurizable fluid systems having aluminum or galvanized wetted parts. Prolonged exposure to water at elevated temperatures (140°F/60°C) may cause noticeable hydrolysis. May react violently or explode upon contact with alkali or chemically active metals such as finely powdered aluminum, magnesium, potassium and/or sodium.

III. STABILITY

Stable at ambient temperatures and atmospheric pressure. However, exposure to high temperature sources (such as open flame and welding arcs) causes thermal-oxidative decomposition yielding toxic phosgene gas and corrosive hydrogen chloride.

IV. FIRE HAZARD

Methylene chloride does not have a measurable flash point by conventional test methods. It is not considered flammable but forms flammable vapor/air mixtures at approximately 212°F (100°C) or higher. Under fire conditions, decomposes to form toxic phosgene gas and corrosive hydrogen chloride.

V. FIREFIGHTING TECHNIQUE

Vapors are irritating to the respiratory tract and may cause breathing difficulty and pulmonary edema. Symptoms may be delayed several hours or longer depending upon the extent of exposure.

As in any fire, prevent human exposure to fire, smoke, fumes or products of combustion. Evacuate nonessential personnel from the fire area. Firefighters should wear full-face, self-contained breathing apparatus and protective clothing.

Use standard firefighting techniques to extinguish fires involving this material—use water spray, dry chemicals or carbon dioxide.

If not leaking, use a water spray to keep fire-exposed containers cool to prevent rupture due to excessive heat. High pressure water hose may spread product from broken containers increasing contamination or fire hazard.

VI. HUMAN HEALTH

WARNING: Vapor and liquid may be harmful if inhaled, swallowed, or absorbed by skin. Avoid prolonged or repeated breathing of vapor. May cause skin and eye irritation. Avoid contact with skin, eyes, and clothing.

The primary route of entry for methylene chloride is inhalation.

Inhalation of large amounts of the vapor may cause nausea, chills, headache, lightheadedness, drowsiness, and irritation of the respiratory tract. Continued overex-

Stauffer CHEMICALS
STAUFFER CHEMICAL COMPANY
BASIC PRODUCTS GROUP
Westport, Connecticut 06881

posure may produce unconsciousness, kidney and lung damage, and death.

Eye irritation and blurred vision may result from eye contact by the liquid or large quantities of the vapor.

Proionged skin contact with the liquid may cause burns. Repeated skin exposures may produce dermatitis.

LONG TERM EXPOSURE: An epidemiological study performed on a large group of male workers at an Eastman Kodak facility in New York, who were continuously exposed to estimated TWA exposures of 30 - 125 ppm of methylene chloride for up to 30 years, has been reported. There was no increase in mortality among exposed workers as compared to industrial controls and the general New York State male population. (1)

VII. TOXICOLOGY

Ingestion

The acute oral LD50 is 2,710 mg/kg in male rats and 2,330 mg/kg in female rats. A single oral dose of 2,150 mg/kg produced mild depression and 20 percent mortality in male rats, and produced moderate to severe depression, tremors and 40 percent mortality in female rats. A single oral dose of 4,640 mg/kg resulted in dyspnea, ataxia, and narcosis in female rats and 100% mortality in male and female rats.

Skin Contact

The acute dermal LD50 is greater than 4,640 mg/kg in rabbits. A single dermal application of 4,640 mg/kg did not produce signs of toxicity in male or female rabbits. Local effects included a mild erythema and moderate edema.

Mild to moderate irritant to rabbit skin following a 4-hour exposure.

Eye Contact

A single ocular dose of 0.1 mL produced lacrimation, inflammation, conjunctival edema, and an increased corneal thickness (reversible). (2)

Inhalation

The acute inhalation LC50 is greater than 19.5 mg/L (nominal concentration) in both male and female rats. A single 1-hour inhalation exposure of 19.5 mg/L (nominal concentration) produced slight depression, moderate ataxia, and ocular protrusion. The acute inhalation LC50 in mice is approximately 14,400 - 17,400 ppm. Seven hour exposures to doses ranging from 13,000 - 17,000 ppm produced ataxia, labored respiration, muscular twitching, and narcosis. (3)

Monkeys, dogs, rabbits, guinea pigs and rats exposed to 500 ppm for 8 hour/day, 5 days/week, for 15 weeks showed 20% mortality (in rats), and a slight increase in eosinophils (rabbits). (3)

Monkeys, dogs, rats, and mice were continuously exposed to 25 or 100 ppm for 100 days. No overt signs of stress were observed. The exposure produced: histopathological effects in mouse livers (100 ppm) and rat kidneys (25 and 100 ppm); no significant findings in hematology, clinical chemistry or histopathology in dogs and monkeys; and significantly increased carboxyhemoglobin in dogs and monkeys (monkeys 100 and 25 ppm, dogs 100 ppm). (3)

Rats and hamsters were exposed by inhalation to 0, 500, 1,500 or 3,500 ppm of methylene chloride for 6 hours per day, 5 days a week for 2 years. No organ-specific toxicity was observed in hamsters. Carboxyhemoglobin levels were elevated in hamsters and rats at all dose levels, but this effect was not cumulative. (4)

Histopathological effects in the liver were observed in male and female rats at all dose levels and considered to be exposure-related. Despite these effects, there was no increase in neoplastic (hyperplastic) liver nodules and no increase in hepatocellular carcinomas. (4)

Increased total numbers of benign mammary tumors were seen in male and female rats, but no increase in malignant mammary tumors was observed. There were no significant lung tumor findings in any exposed group compared to the controls. (4)

Male rats in the 3,500 ppm dose group exhibited a significant increase in sarcomas in or around the salivary glands. A significant increase in this finding was not observed in males exposed at 500 or 1,500 ppm or any of the exposed females. (4)

In a second study, male and female rats were exposed to 0, 50, 200, or 500 ppm for 6 hrs/day, 5 days/week for 2 years. Additionally, one group of females was exposed at 500 ppm for the first 12 months only, and another group for the second 12 months only. (5)

A significant increase in histopathological effects in the liver was observed in females exposed to 500 ppm for 2 years and to 500 ppm for the first 12 months. (5)

Mutagenicity

Methylene chloride was examined for mutagenic activity in *in vitro* microbial assays, with and without metabolic activation, using the TA-100 and TA-98 strain of *Salmonella typhimurium* as the indicator organism. The compound demonstrated mutagenic activity in both assays. (6)

Methylene chloride did not induce chromosomal aberrations in a rat bone marrow assay. (4)

Methylene chloride induced cellular transformation in Fischer rat embryo cells. (7)

T-4054, T-4171, T-5628

VIII. FIRST AID

CALL A POISON CENTER OR
A PHYSICIAN IMMEDIATELY.

If a known exposure occurs or is suspected, immediately start the recommended procedures below. Simultaneously contact a Poison Center, a physician or the nearest hospital. Inform the person contacted of the type and extent of exposure, describe the victim's symptoms, and follow the advice given.

NOTE TO PHYSICIAN

Methylene chloride is metabolized to carbon monoxide and carbon dioxide. The resultant elevation of carboxyhemoglobin levels is of short duration (e.g. usually less

(1) J. Occ. Med. 20 (10):657 (1978).
(2) Toxicol. 6:173-187 (1976).
(3) HEW (NIOSH) Publication No. 76-138.
(4) Burek, J. D. et. al (1980) Methylene Chloride: "A Two-Year Inhalation Toxicity and Oncogenicity Study in Rats and Hamsters." Final Report Issued December 31, 1980 by Dow Chemical, USA.
(5) Nitschke, K. D. et. al (1982) Methylene Chloride: "A Two-Year Toxicity and Oncogenicity Study." Final Report Issued October 11, 1982 by Dow Chemical, USA.
(6) Mut.Res. 56:245-248 (1978)
(7) In Vitro 14:290-293 (1978)

than 48 hours) unless overexposure is prolonged. Inhalation of large amounts of methylene chloride may cause pulmonary edema and could be fatal. Exposure to high concentrations of methylene chloride may cause depression of the central nervous system.

FOR ADDITIONAL MEDICAL OR TOXICOLOGICAL INFORMATION, CALL COLLECT, DAY OR NIGHT, STAUFFER CHEMICAL COMPANY (203) 226-6602 OR CHEMTREC (800) 424-9300.

Ingestion
If swallowed, immediately give several glasses of water but *do not* induce vomiting. If vomiting does occur, give fluids again. Have a physician determine if condition of patient will permit induction of vomiting or evacuation of stomach. Do not give anything by mouth to an unconscious or convulsing person.

Skin Contact
Immediately flush all affected areas with large amounts of water for at least 15 minutes while removing any contaminated clothing and shoes. Do not attempt to neutralize with chemical agents. Get medical attention immediately. Wash clothing before reuse.

Eye Contact
Immediately flush the eyes with large quantities of running water for a minimum of 15 minutes. Hold the eyelids apart during the flushing to ensure rinsing of the entire surface of the eye and lids with water. Do not attempt to neutralize with chemical agents. Obtain medical attention as soon as possible. Oils or ointments should not be used. Continue the flushing for an additional 15 minutes if the physician is not immediately available.

Inhalation
Remove from contaminated atmosphere. Seek medical attention if respiratory irritation occurs. If the breathing becomes difficult, oxygen may be delivered from a demand-type or continuous flow inhaler, preferably with a physician's advice. If not breathing, give artificial respiration, preferably mouth-to-mouth. Get medical attention.

IX. INDUSTRIAL HYGIENE

Ingestion
All food should be kept in a separate area away from the storage/use location. Eating, drinking and smoking should be prohibited in areas where there is a potential for significant exposure to this material: Before eating, hands and face should be thoroughly washed.

Skin Contact
Skin contact with liquid or its aerosol should be prevented through the use of suitable protective clothing, gloves and footwear selected with regard for use condition exposure potential.

Eye Contact
Eye contact with liquid or its aerosol should be prevented through the use of chemical safety glasses, goggles or a face shield selected with regard for use condition exposure potential.

Inhalation
If use conditions generate airborne liquid, aerosol or vapor handle this material only in an open (e.g., outdoor) or well ventilated area. Where adequate ventilation is not available, use NIOSH-approved organic vapor respirators to reduce exposure. Where exposure potential under the use conditions necessitates a higher level of protection, use a positive-pressure, air-supplied respirator.

Exposure Limits
The Federal OSHA Permissible Exposure Limit (PEL) is an 8-hour, time-weighted average of 500 ppm (1,700 mg/m^3) and a ceiling concentration of 1,000 ppm for methylene chloride. (8)

The American Conference of Governmental Industrial Hygienists (ACGIH) has recommended a Threshold Limit Value (TLV) of 100 ppm (360 mg/m^3) as an 8-hour time-weighted average, and a Short Term Exposure Limit (STEL) of 500 ppm (1,700 mg/m^3) for methylene chloride. (9)

X. SPILL HANDLING

Make sure all personnel involved in the spill cleanup follow good industrial hygiene practices (refer to SECTION IX: INDUSTRIAL HYGIENE). Any person entering a significant spill area or an unknown concentration of a gas or vapor, should wear a positive-pressure, self-contained breathing apparatus or a positive-pressure, supplied-air respirator with escape pack.

Small spills can be handled routinely. Use adequate ventilation and wear a respirator to prevent inhalation exposure. Wear protective clothing to prevent skin and eye contact. Use the following procedures:

Evacuate spill area and remove sources of combustion or extreme heat. Ventilate the area and let small spills evaporate. Somewhat larger spills should be contained and recovered where possible. Mop up spilled methylene chloride or adsorb with a suitable adsorbent such as clay, sawdust or kitty litter. Reclaim waste solvent by distillation procedures or offer for disposal to a licensed hydrocarbon solvent reclaimer.

Large spills should be handled according to a predetermined plan. For assistance in developing a plan, contact Stauffer Chemical Company, Westport, CT 06881.

IN CASE OF SPILL EMERGENCY, DAY OR NIGHT, CALL (800) 424-9300 CHEMTREC.

XI. CORROSIVITY TO MATERIALS OF CONSTRUCTION

In the absence of contamination by water or moisture, methylene chloride is not corrosive to common materials such as copper, iron or stainless steel. In contact with water or moisture, particularly at elevated temperatures, it can be corrosive. Methylene chloride may soften or dissolve certain plastics and rubbers. Avoid contact with alkali or chemically active metals because an explosion may occur (See SECTION II: CHEMICAL REACTIVITY).

(8) 29 CFR 1910.1000
(9) The American Conference of Governmental Industrial Hygienists (ACGIH). 1982. *Threshold Limit Values for chemical substances and physical agents in the workroom environment with intended changes for 1982.* ACGIH: Cincinnati, Ohio.

XII. STORAGE REQUIREMENTS

Containers should be stored in a cool, dry, well ventilated area away from flammable materials and sources of heat or flame. Store away from foodstuffs or animal feed. Exercise due caution to prevent damage to or leakage from the container.

Avoid airborne concentration buildup. No smoking where vapors of this material are present. Open containers with caution.

When methylene chloride vapors are drawn into the combustion chamber of a space heater, even at low levels, severe corrosion damage to the heater can occur.

XIII. DISPOSAL OF UNUSED MATERIAL

Material that cannot be used or chemically reprocessed should be disposed of at an approved facility in accordance with any applicable regulations under the Resource Conservation and Recovery Act.

NOTE: State and local regulations may be more stringent than Federal.

Contact the nearest Stauffer Sales Office for assistance in disposing of unused material. Waste material can be sent to a licensed hydrocarbon solvent reclaimer.

XIV. DISPOSAL OF CONTAINER

Dispose of empty containers according to any applicable regulations under the Resource Conservation and Recovery Act.

NOTE: State and local regulations may be more stringent than Federal.

XV. ENVIRONMENTAL PRECAUTIONS

Avoid runoff to sewers.

Chevron

Chevron Environmental Health Center, Inc.
A Chevron Research Company Subsidiary
15299 San Pablo Avenue, Richmond, California
Mail Address: P.O. Box 4054, Richmond, CA 94804

R. D. Cavalli
Manager
Product Evaluation

3/3 Lynne pls write to staff person working on MC

February 24, 1986

Methylene Chloride

William V. Loscutoff, Chief
Toxic Pollutants Branch
California Air Resources Board
P.O. Box 2875
Sacramento, California 95812

Dear Mr. Loscutoff:

As per your request, in accordance with Health and Safety Code Sections 39650, et seq., we have reviewed our files on the health effects of methylene chloride. We have no relevant "in-house" data on methylene chloride, but feel the following references may be useful additions to the bibliography for the Department of Health Services:

1. Heppel, L. A., Neal, P. A., Perrin, T. L., Orr, M. L., Porterfield: Toxicology of Dichloromethane (Methylene Chloride). I. Studies on Effects of Daily Inhalation. J. Ind. Hyg. Toxicol. 26: 8-16, 1944.

2. Heppel, L. A., Neal, P. A.: Toxicology of Dichloromehtane (Methylene Chloride). II. Its Effect Upon Running Activity in the Male Rat. J. Ind. Hyg. Toxicol. 26: 17-21, 1944.

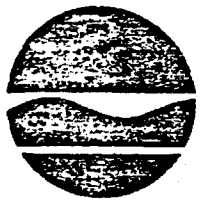
Thank you for the opportunity to contribute to the review of candidate toxic air contaminants.

Sincerely,

RD Cavalli /GFSH

MAR 03 1986

New York State Department of Environmental Conservation
50 Wolf Road, Albany, New York 12233-0001



Henry G. Williams
Commissioner

March 7, 1986

RECEIVED

MAR 11 1986

Stationary Source
Division
Air Resources Board

Mr. Peter Venturini
Chief
Stationary Source Division
State of California
Air Resources Board
1102 Q Street
P. O. Box 2815
Sacramento, California 95812

Dear Mr. Venturini:

This is in response to your letter of February 5, 1986 in which you requested information on the health effects of methylene chloride. At this time, we are conducting a quantitative risk assessment by applying statistical models to the bioassay data obtained from the inhalation study completed by the National Toxicology Program (NTP) in 1985. In addition, we will be completing a search of the same references which were included with your letter.

When we have completed this risk assessment, we will be glad to send you a copy.

Sincerely,

Virginia M. Rest
Environmental Chemist
Section of Toxics Assessment
Bureau of Air Toxics

VMR:cb

ATTACHMENT II

Health Effects References for Methylene Chloride (1/28/1986)

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ATTACHMENT III

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During 1985, the ARB performed sampling for methylene chloride at twenty-two sites in seven air basins. The maximum concentration of methylene chloride measured was 47.0 ppb; the minimum concentration was below the detection limit of 0.6 ppb. Average concentrations at the monitoring stations range from 0.3 ppb at Merced to 5.6 ppb at Santa Barbara. The average concentration for all samples taken during 1985 at five sites in the South Coast Air Basin is 3.7 ppb.

The major uses of methylene chloride are as a paint remover, degreaser, aerosol propellent, and foam blowing agent. Potential point sources are vapor degreasing and cold cleaning solvent operations, polyurethane foam production facilities, and photo resist stripping operations associated with the electronics industry. Widespread emissions of methylene chloride occur through its use in consumer products such as aerosol sprays and paint and varnish removers.

State of California

Department of Health Services

Memorandum

To : James Boyd
Executive Officer
Air Resources Board
1102 Q Street
Sacramento, CA 95814

Date : September 29, 1986

Subject: Request for Extension of Methylene Chloride Evaluation

From : Office of the Director
714 P Street, Room 1253
Sacramento, CA
5-1248

We are unable to complete the AB 1807 document on methylene chloride due on July 15, 1986. Therefore, we are requesting the statutory 30-day extension plus an additional 60 days to October 13, 1986. Much of this document has been performed under contract. Department staff have requested the contractor to make extensive changes to the draft, which necessitates the need for this extension.

Kenneth W. Kizer, M.D., M.P.H.
Director